PB86-198371

Assessment of Solid Waste Characteristics and Control Technology for Oil Shale Retorting

Monsanto Co., Dayton, OH

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

May 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-198371

EPA/600/7-86/019
May 1986

ASSESSMENT OF SOLID WASTE CHARACTERISTICS AND CONTROL TECHNOLOGY FOR OIL SHALE RETORTING

by

Ashok K. Agarwal

Monsanto Company
1515 Nicholas Road
Dayton, Ohio 45418

Contract No. EPA 68-01-6487

EPA Project Officer:

Edward R. Bates
Air and Energy Engineering Research Laboratory
Research Triangle Park, North Carolina 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/7-86/019	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Assessment of Solid Waste Characteristics and Control Technology for Oil Shale Retorting		5. REPORT DATE May 1986 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) A.K. Agarwal		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Company 1515 Nicholas Road Dayton, Ohio 45418		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-01-6487
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 9/83 - 2/85 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is Edward R. Bates (EPA, HWERL, Cincinnati, OH 45268, 513/684-7774).

16. ABSTRACT

The report presents information on oil shale deposits in the eastern and western parts of the United States, their geological subdivisions, locations, tonnage, and physical and chemical characteristics. Characteristics of solid and liquid wastes produced from various oil shale processing technologies and control methods are presented. Also included are results from an experimental study to construct liners and covers for disposal of spent shale. A compilation of available data on the autoignition potential of raw and spent shales indicates a similarity between raw shale fines and bituminous coals.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Properties	Pollution Control	13B	
Oil Shale	Analyzing	Stationary Sources	08G	
Wastes	Linings	Retorting	14G	11G
Waste Disposal	Coverings	Solid Waste		11C
Assessments		Characterization	14B	
Autoignition			21B	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 354
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE $28.95

EPA Form 2220-1 (9-73)

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract 68-01-6487 to Monsanto Company. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

ABSTRACT

This report is a comprehensive study of the characteristics of solid and liquid wastes produced from various oil shale processing technologies, and control methods for environmentally safe disposal of solid wastes. It also includes the results from an experimental study to construct liners and covers for proper disposal of spent shales. In addition the auto ignition potential of raw and spent shales has been evaluated.

Considerable effort is currently being directed to commercialization of processes to produce liquid fuels from oil shale deposits in the United States. When financing uncertainties are resolved, construction of large-scale plants could begin. The retorting of oil shale produces large quantities of solid wastes. These wastes include raw mined oil shale (which does not contain enough kerogen for economical recovery), spent oil shale (mineral matter from which the kerogen has been thermally removed by retorting), overburden material (which must be removed before the shale can be mined), shale fines from processing operations (e.g., dust collected in fabric filters) and process wastes (e.g., spent catalysts, wastewater treatment sludges).

Oil shale deposits in the eastern and western parts of the United States, their geological subdivisions, their locations, tonnage, and their physical and chemical characteristics have been described. The solid and liquid wastes generated from the various oil shale technologies have been compiled. Amounts of solid and liquid wastes generated and their composition depend, among other things, on the particular technology used and on the type of shale processed. Some of the wastes may also be site specific. Available field and laboratory leachate data are also presented.

If only one-half of the planned production comes on line, it would eventually amount to approximately 600,000 barrels per day of shale oil. This would lead to approximately 740,000 tons/day or 270 million tons per year of retorted oil shale, along with lesser quantities of other solid wastes, which will require environmentally safe disposal. If not properly managed, these high volume wastes are capable of producing leachates that could contaminate the water supply for millions of people. Surface disposal sites covering many square miles in area and hundreds of feet in depth would do extensive property damage and threaten lives should they ever suffer sudden mass failure. An experimental program

was undertaken to establish the best combination of spent shale with materials readily available at the disposal site to construct liners and covers for the spent shale disposal.

Also in this report available information has been compiled in order to evaluate the auto ignition potential of raw and spent shales from various oil shale processes. The results indicate that raw shale fines have a potential for spontaneous ignition similar to bituminous coals while such potential for retorted shales appear to be less. Hence, there is a potential that if oil shale disposal sites are not properly designed they could auto ignite. It appears probably that control technology employed by the coal industry can be modified and applied to oil shale disposal sites to mitigate this hazard.

Control technologies to prevent serious adverse impacts from disposal of billions of tons of oil shale wastes have been proposed but their application to oil shale waste materials on the scale required for commercial plants has not been demonstrated. Furthermore, to be effective, these control technologies must be applied to highly technical and integrated disposal designs that are site and process specific. There is no current experience in disposal of wastes of similar composition or of volumes approaching that which will result from the oil shale industry.

CONTENTS

Abstract. iii
Figures vii
Tables. x
Acknowledgment. xx

1. Introduction 1
    1.1 Sources and volumes of solid waste, including an overview of the oil shale industry . . . 1
    1.2 Potential dangers to human health and the environment from the disposal and reuse of the wastes. 5
    1.3 Present/proposed disposal approaches. 17
    1.4 Conclusions and additional research needed. . 21

2. Characteristics Of U.S. Oil Shale. 23
    2.1 Introduction. 23
    2.2 Location. 23
    2.3 Geology 28
    2.4 Composition 41
    2.5 Physical properties 52

3. Solid Wastes and Their Characteristics for Oil Shale Retorting Processes 69
    3.1 Lurgi-Ruhrgas oil shale retorting 69
    3.2 TOSCO II oil shale retorting. 85
    3.3 Paraho direct heating mode oil shale retorting 105
    3.4 Paraho indirect heating mode oil shale retorting 127
    3.5 Occidental modified *in situ* oil shale retorting 136
    3.6 T^3 oil shale retorting. 151
    3.7 Hytort oil shale retorting. 155
    3.8 Geokinetics horizontal *in situ* oil shale retorting 164
    3.9 Superior circular grate oil shale retorting . 168
    3.10 Union Oil A oil shale retorting. 177
    3.11 Union Oil B oil shale retorting. 182
    3.12 Union Oil SGR oil shale retorting. 191
    3.13 Chevron STB oil shale retorting. 202
    3.14 Allis-Chalmers oil shale retorting 210
    3.15 Dravo oil shale retorting 216

CONTENTS (continued)

4. Environmental Control Technologies 219

4.1 Environmental impacts. 219
4.2 Disposal alternatives. 222
4.3 Control technologies 227

References. 255
Appendix. A-1

A. Auto-oxidation potential of raw and spent shale and the suggested design of piles to avoid the auto-ignition of shales. A-1
B. Use of spent oil shale as a liner material at spent shale disposal sites . . . . B-i

FIGURES

Number		Page
2.2-1	Principal United States oil shale deposits. . .	24
2.2-2	Green River formation oil shales-Utah, Colorado, and Wyoming	25
2.2-3	Distribution of upper Devonian and lower Mississippian Black Shales in the Eastern United States	27
2.3-1	Schematic North-South cross section of Piceance Creek showing relationship of oil shale bearing members of the Green River formation and surrounding strata.	32
2.3-2	Schematic cross section of Uinta Basin showing relationship of oil shale bearing Green River formation with surrounding strata	34
2.3-3	Schematic cross section showing relationship of Green River formation with surrounding strata	37
2.3-4	Oil yield of Tipton shale member.	38
2.3-5	Oil yield of Wilkins peak member.	39
2.3-6	Oil yield of Laney shale member	40
2.4-1	Organic matter content of Green River oil shales.	44
2.5-1	Specific gravity and oil yield of Colorado oil shales.	54
2.5-2	Compressive strength of oil shales.	60
2.5-3	Compressive strength versus Fischer assay of Colorado oil shale, Anvil Points Mine	62
3.1-1	Lurgi-Ruhrgas oil shale retorting process . . .	70
3.1-2	Lurgi-Ruhrgas Process operations and waste streams	72

FIGURES (continued)

Number Page

3.2-1 TOSCO II oil shale retorting process. 86

3.2-2 Process block flow diagram for sand wash processing facility 88

3.3-1 Schematic of Paraho direct heating mode process 106

3.3-2 Paraho commercial process flowsheet 107

3.4-1 Paraho indirect mode process flow diagram . . . 128

3.5-1 Schematic of the Occidental modified *in situ* retorting process 136

3.5-2 Occidental MIS retorting, oil/water separation and steam stripping 137

3.6-1 T^3 retorting process. 152

3.7-1 Diagram of IGT oil shale gasification process development unit. 156

3.7-2 Hytort commercial plant conceptual design . . . 158

3.8-1 Geokinetics horizontal *in situ* retort. 163

3.8-2 Electrical conductivity breakthrough curve for Leachate from Geokinetics spent shale . . 167

3.9-1 Superior retorting process retort showing movement of charge through various zones. . . 170

3.9-2 Superior direct-heated process. 171

3.9-3 Superior process flow diagram and major waste streams 172

3.10-1 Diagram of Union Oil Retort A 178

3.11-1 Flow diagram for retort system in Union oil Retort B prototype plant. 183

3.11-2 Block flow diagram for Union oil Retort B prototype plant 185

3.12-1 Diagram of Union Oil SGR-3 retorting process. . 192

3.13-1 Process flow scheme of Chevron STB retort . . . 203

FIGURES (continued)

Number		Page
3.13-2	Block flow diagram of Chevron semiworks oil shale plant	206
3.14-1	Allis-Chalmers oil shale process flowsheet. . .	213
3.14-2	Allis-Chalmers oil shale retorting and combustion process development unit flow schematic	214
3.15-1	Dravo retorting process	216
3.15-2	Dravo pilot plant flowsheet schematic	218
4.3-1	Surface hydrology control technologies.	228
4.3-2	Runon diversion costs	231
4.3-3	Runoff collection costs	233
4.3-4	Runoff/leachate pond costs.	235
4.3-5	Runoff/leachate pond liner costs.	236
4.3-6	Subsurface hydrology control technologies . . .	237
4.3-7	Liner costs	240
4.3-8	Leachate collection costs	242
4.3-9	Groundwater collection costs.	244
4.3-10	Surface stabilization technologies.	245
4.3-11	Dust control costs.	248
4.3-12	Reclamation and revegetation costs.	250

TABLES

Number		Page
1.1-1	SFC Oil Shale Projects.	2
1.1-2	Non SFC Sponsored Oil Shale Projects.	3
1.1-3	Approximate Solid Waste Relationships	6
1.1-4	Major Waste Produced Over a Period of 20 Years (TOSCO II 47,000 bbl/day plant with upgrading)	7
1.2-1	Summary of Results from Differential Scanning Calorimetry and Nonadiabatic Oxygen Absorption Testing.	8
1.2-2	Chemical Properties of Union B Retorted Shale .	9
1.2-3	Estimated Composition of Process Water for Retorted Shale Cooling/Wetting.	10
1.2-4	RCRA Testing of Simulated Shale Plant Wastes (Union B Process)	11
1.2-5	Chemical Composition of Leachates from Union B Retorted Shale (mg/L)	12
1.2-6	Retorted Shale Leachates by Leaching Method (mg/L).	13
1.2-7	Raw Mined Oil Shales Leachates (Maximum Observed Concentrations).	14
1.2-8	Estimated Quantities of Some Major Constituents Leachable from Oil Shale (Assuming Permeability and Water Availability are not Limiting Factors)	16
1.3-1	Key Features of Solid Waste Disposal Approaches	18
2.2-1	Total In-Place Shale Oil Resources of the Green River Formation	25

TABLES (continued)

Number		Page
2.4-1	Mineral Content of Green River Oil Shale Versus Grade	41
2.4-2	Average Mineral Composition of Mahogany Zone Shale, Colorado and Utah	41
2.4-3	Fischer Assay Data of the Inorganic Mineral Portions of 16 Samples of Green River Oil Shale Ranging From 10.5 To 75.0 gal/ton Oil Shale	42
2.4-4	Chemical Composition of the Inorganic Portion of Various Grades of Green River Oil Shale and of The Spent Shale Products	43
2.4-5	Typical Mineralogical Composition of Devonian Black Shale	43
2.4-6	Probable Composition of Mahogany-Zone Organic Matter	45
2.4-7	Elemental Composition of New Albany Shale Organic Matter	45
2.4-8	Approximate Carbon/Hydrogen Ratios in Various Organic Materials	46
2.4-9	Authigenic Sodium Minerals In The Green River Formation	48
2.4-10	Average Distribution of Sulfur and Nitrogen In Oil Shale	50
2.4-11	Distribution of Sulfur and Nitrogen in Colorado Oil Shale	50
2.4-12	Levels of Trace Elements in Green River Oil Shale	51
2.5-1	Visual Features of Green River Oil Shale	53
2.5-2	Weight (Inplace) and Weight (Broken) for Green River Oil Shale	56
2.5-3	Porosities of Raw and Thermally Treated Oil Shales (Percent of Bulk Volumes)	57

TABLES (continued)

Number		Page
2.5-4	Shear Strengths of Lean Oil Shale Specimens from Roof Material of USBM Experimental Mine (Anvil Points).	58
2.5-5	Compressive Strengths of Raw and Thermally-Treated Oil Shales (Kilograms Per Square Centimeter)	59
2.5-6	Compressive Strength of Green River Oil Shale Samples Cut Perpendicular to Bedding (Samples from USBM Experimental Mine, Anvil Points, Colorado)	61
2.5-7	Summary of the Range of Concentrations in Leachate Samples.	63
2.5-8	Comparison of Trace Element Concentrations from Raw Mined Shale with those from Soils and Previously Exposed Shales	64
2.5-9	Mean Values for Major Ion Composition of C-a Leachate.	65
2.5-10	Mean Values for Major Ion Composition of C-b Leachate.	65
2.5-11	Mean Values of Trace Element Concentrations of C-a Leachate.	67
2.5-12	Mean Values of Trace Element Concentrations of C-b Leachate.	67
2.5-13	Maximum Observed Concentrations in Raw Shale Leachates	68
3.1-1	Inventory of Streams to be Disposed of as Solid Waste in the Lurgi-Ruhrgas Process. . .	75
3.1-2	Physical Properties of Lurgi Processed Shale. .	77
3.1-3	Summary of Hydraulic Conductivity Measurements for Various Compaction and Loadings for Lurgi Retorted Shale.	78
3.1-4	Water Holding Capacity of Lurgi Processed Shales at Various Pressures and Bulk Densities	78

TABLES (continued)

Number Page

3.1-5 Composition of Lurgi Processed Moisturized Shale 79

3.1-6 Inorganic Analysis of the Lurgi Processed Shale 79

3.1-7 Major Ion Composition of Column Leachate-Lurgi Retorted Shale. 80

3.1-8 Concentration of Selected Trace Elements in Column Leachate of Lurgi Retorted Shale . . . 81

3.1-9 Concentrations in ASTM Water Shake Test Extracts - Lurgi Spent Shales 82

3.1-10 Concentrations in RCRA Test Extracts - Lurgi Spent Shales. 83

3.1-11 Leachable Mass as Indicated by the ASTM Proposed Water Shake Test for Lurgi Spent Shales - mg/g 84

3.1-12 Leachable Mass as Indicated by the RCRA Extraction Test for Lurgi Spent Shales - mg/g 84

3.2-1 Summary of Solid Wastes Generated at Sand Wash Processing Facility 90

3.2-2 Major Waste Produced Over a Period of 20 Years for TOSCO II 47,000 bbl/day Plant with Upgrading 91

3.2-3 Physical Properties of TOSCO II Processed Shale 92

3.2-4 Sieve Analysis of TOSCO II Spent Oil Shale Residue 92

3.2-5 Hydraulic Conductivity Measurements of TOSCO II Retorted Shale. 93

3.2-6 Water Holding Capacity of TOSCO II Processed Shales at Various Pressures and Bulk Densities 93

3.2-7 Reported Analysis of TOSCO II Processed Shale . 94

3.2-8 Selected Elemental Concentrations in Raw and Retorted TOSCO II Oil Shales. 94

TABLES (continued)

Number Page

3.2-9 Some Polycyclic Aromatic Hydrocarbons that have been Detected in the Benzene Extract of TOSCO II Spent Shales 95

3.2-10 Approximate Composition of TOSCO II Combined Process Wastewater (50,000 bbl/day upgraded shale oil production) 96

3.2-11 Organic Content of Gas Condensate (Foul Water) For TOSCO II. 97

3.2-12 Composition of Foul Water for TOSCO II. 97

3.2-13 Inorganic Species in TOSCO II Foul Water. . . . 98

3.2-14 Concentrations in ASTM Water Shake and RCRA Extracts - TOSCO II Spent Shales. 99

3.2-15 Leachable Mass as Indicated by RCRA and ASTM Water Shake Extraction Test for TOSCO II Spent Shales. 100

3.2-16 Effluent Concentrations - (TOSCO II) Spent Shales. Constant Rate Injection into a Dry Column. 101

3.2-17 Levels of Trace Elements Measured in Runoff and Leachates from Field Test Plots of TOSCO II Retorted Shale (ppm). 102

3.2-18 Inorganic Composition of TOSCO II Leachates Produced During Laboratory and Field Lysimeter Studies (mg/L). 103

3.3-1 Paraho Direct Solid Wastes: Types and Quantities. 110

3.3-2 Paraho Direct Retorted Shale Characteristics. . 111

3.3-3 Paraho Direct Retorted Shale Major Elements (wt. %) 112

3.3-4 Paraho Direct Retorted Shale Trace Elements (ppm) 113

3.3-5 Paraho Direct Product Water Bulk Properties (wt. %). 115

TABLES (continued)

Number Page

3.3-6 Paraho Direct Product Water Major Species/Gross Salinity (ppm). 116

3.3-7 Paraho Direct Product Water Trace Elements (ppm). 118

3.3-8 Compounds Identified in Paraho Direct Oil Shale Wastewaters 119

3.3-9 Paraho Direct Recycle Gas Line Drain (ppm). . . 121

3.3-10 Concentrations in RCRA and Water Shake Test Extracts - Paraho Direct Spent Shales 122

3.3-11 Leachable Mass as Indicated by the ASTM Proposed Water Shake Extraction Test for Paraho Direct Spent Shales - mg/g 123

3.3-12 Column Leaching Effluent Concentrations for Paraho Direct Spent Shales 124

3.3-13 Inorganic Composition of Paraho Direct Spent Shale Leachates Produced During Field Lysimeter Studies, (mg/L) 125

3.4-1 Paraho Indirect Retorted Shale Characteristics 130

3.4-2 Paraho Indirect Retorted Shale Chemical Composition 131

3.4-3 Composition of Paraho Indirect Spent Oil Shales 132

3.4-4 Paraho Indirect Process Water Composition . . . 133

3.4-5 Inorganic Analysis of Condensate Streams from the Paraho Indirect Process 134

3.4-6 Composition of Batch Generated Leachate from Paraho Indirect Retorted Shale. 135

3.5-1 Inventory of Solid and Liquid Waste Streams for Occidental MIS Process. 140

3.5-2 Compositions of Solid and Waste Streams for Occidental MIS Process. 141

3.5-3 Composition of MIS Occidental Processed Shale . 142

TABLES (continued)

Number Page

3.5-4 Boron and Fluoride in Oxy Retort 3E Spent Shale 142

3.5-5 Mineralogical Analyses for Selected Samples of Oxy Retort 3E Spent Shale Core. 142

3.5-6 Analysis of Core Samples from Oxy Retort 3E Preliminary Data. 143

3.5-7 Oxy Retort 6 Steam Boiler Blowdown Collected - March 6, 1979 (in ppm except as noted). . . . 144

3.5-8 Compounds Identified in Occidental Oil Shale Retort Wastewaters. 145

3.5-9 Oxy Retort 6 Product Water Analysis Results . . 147

3.5-10 Concentrations of Dissolved Species in the Leachate from Occidental MIS Processed Shale. 148

3.5-11 Concentration Range of Macro Ions Found in the First Fraction of Leachates from Occidental MIS Retorted Shale. 148

3.5-12 Inorganic Composition of Leachates from Occidental's Retort 3E, Logan Wash, Colorado (mg/L). 149

3.7-1 Water Holding Capacity of Hytrot Processed Shales at Various Pressures and Bulk Densities 159

3.7-2 Concentrations in ASTM Water Shake and RCRA Tests Extracts - Hytort Spent Shales. 160

3.7-3 Leachable Mass from Hytort Shale as Indicated by the ASTM Proposed Water Shake Test and RCRA Extraction Test - mg/g 161

3.8-1 Inorganic Composition of Leachates from Geokinetics Spent Shale (mg/L). 164

3.8-2 Major Ion Composition of Effluent (Geokinetics 6). 165

3.8-3 Concentration (mg/L) of Trace Elements for Selected Pore Volumes (Geokinetics 6) 166

TABLES (continued)

Number		Page
3.9-1	General Water Quality Parameters of Superior Oil Shale Process Water	173
3.9-2	Inorganic Composition of Superior Leachate Produced by the ASTM Test Method D3987. . . .	174
3.9-3	The Effect of Coproducted Retort Waters on the Quality of Superior Leachates from Spent Shales.	175
3.9-4	Effect of Distilled Water, and Time on the Leachate Quality of Moistened, Compacted Superior Spent Shales	176
3.9-5	Concentration of Metals in Leachates from Superior Retorted Shales.	176
3.10-1	Physical Properties of Union A Spent Shale. . .	180
3.10-2	Chemical Properties of Union A Retorted Shale .	180
3.10-3	Analysis of Leachate Obtained in Laboratory Tests of Union A Raw and Retorted Shale . . .	181
3.10-4	Inorganic Composition of Leachates from Union A Spent Shale	181
3.11-1	Inventory of Streams to be Disposed of as Solid Wastes in Union B Process	186
3.11-2	Physical Properties of Union B Spent Shale. . .	187
3.11-3	Chemical Properties of Union B Retorted Shale .	187
3.11-4	Estimated Composition of Union B Process Water In the Active Basin and the Reuse Water Sump.	188
3.11-5	Inorganic Composition of Leachates from Union B Spent Shale, mg/L	189
3.11-6	RCRA Testing Of Simulated Union B Oil Shale Plant Wastes.	190
3.12-1	Physical Properties of Union SGR Spent Shale. .	193
3.12-2	Particle Size, pH, and Electrical Conductivity of Spent Oil Shales Produced by Union SGR Retorting Process	193

TABLES (continued)

Number		Page
3.12-3	Chemical Properties of Union SGR Retorted Shale	194
3.12-4	Amounts and Quality of Surface Runoff from Union SGR Decarbonized Shale Lysimeter Study.	195
3.12-5	Water Quality of Percolate from Union SGR Decarbonized Shale Lysimeters	196
3.12-6	Analysis of Spring Snowmelt Runoff and Percolate from Union SGR Decarbonized Shale Lysimeter Study. April 21, 1976. . . .	197
3.12-7	Analysis of Runoff and Percolate Samples Collected August 5, 1976 from Union SGR Decarbonized Shale Lysimeter Study.	198
3.12-8	Analysis of Spring Snowmelt Runoff and Percolate from Union SGR Decarbonized Shale Lysimeter Study. April 21, 1976. . . .	199
3.12-9	Analysis of Runoff and Percolate Samples Collected August 30, 1977 from Union SGR Decarbonized Shale Lysimeter Study.	200
3.12-10	Analysis of Spring Snowmelt Runoff and Percolate from Union SGR Decarbonized Shale Lysimeter Study. May 3, 1978	201
3.13-1	Nominal Process Operating Conditions for the Chevron STB Retort.	205
3.13-2	Preliminary Results: Chevron STB Pilot Plant Spent Shale Properties.	208
3.13-3	Chevron STB Spent Shale Leach Test Results. . .	209
3.14-1	Allis-Chalmers Western Shale Tests.	215
4.3-1	Key Features of Surface Hydrology Control Technologies.	229
4.3-2	Key Features of Subsurface Hydrology Control Technologies.	238
4.3-3	Key Features of Surface Stabilization Technologies.	246

TABLES (continued)

Number | | Page
4.3-4 Engineering Costs and Timing of Solid Waste Management Activities for a 47,000 bbl/day Facility (Thousands of Dollars) 252

A-1 Description of Samples Tested by RTI. A-7

A-2 Mean Heat Capacity of Coal and Shale Materials Based on Initial Sample Weight (J/G, -325 Mesh) A-7

A-3 Exothermic Onset Temperature in Oxidation of Coal, Oil Shale and Retorted Oil Shale (2°C/minute heating ramp, -325 Mesh). A-9

A-4 Magnitude of Exothermic Reaction of Coal, Oil Shale and Retorted Oil Shale (2°C/minute heating ramp, -325 Mesh). A-10

A-5 Spontaneous Combustion Index and Calculation Parameters of Materials Subjected to Nonadiabatic Test (Tested Dry). A-12

A-6 Summary of Results From Differential Scanning Calorimetry and Nonadiabatic Oxygen Absorption Testing. A-16

A-7 Effect of Compaction in Reducing the Volume of Air Entering or Leaving a Coal Mass in Response to Barometric Pressure Change. . . . A-18

ACKNOWLEDGMENT

This study and the preparation of this report has involved participation of professionals from Monsanto and independent consultants. Shib C. Chattoraj's work in developing this report is very much appreciated. The contributions of Arthur D. Snyder and Duane R. Day are acknowledged. Also Robert N. Heistand provided valuable review comments. The liner study was performed by Denver Research Institute.

The project is deeply indebted to the EPA Project Officer, Edward R. Bates for his continuing advice and guidance during the course of this effort.

SECTION 1

INTRODUCTION

1.1 SOURCES AND VOLUMES OF SOLID WASTE, INCLUDING AN OVERVIEW OF THE OIL SHALE INDUSTRY

1985 makes the start of the commercial U.S. oil shale industry with the first commercial plant (Union Oil's 10,000 bbl/day Long Ridge facility) coming on line. Many additional and often much larger plants are scheduled to start production between 1987 and 1994 with many of the early plants being subsidized by the Federal Government through the U.S. Synthetic Fuels Corp; (Tables 1.1-1 and 1.1-2). If only one half of the planned production comes on line, it would eventually amount to approximately 600,000 barrels per day of shale oil. Assuming an average shale grade of 30 gal/ton and that 88% of the raw shale retorted will remain as spent shale to be disposed, then about 740,000 tons/day or 270 million tons per year of retorted oil shale, along with lesser quantities of other solid wastes, will require environmentally safe disposal. In addition to retorted oil shale other solid wastes produced will include waste overburden, raw shale fines, shale oil coke, API separator sludges, wastewater treatment sludges, elemental sulfur or sulfur containing wastes from air pollution control equipment, and spent catalysts which may contain highly toxic substances such as arsenic.

The types and quantities of solid wastes that will be produced from proposed oil shale facilities are not well defined at this time. Detailed information prepared as supplements to the Uintah Basin Synfuel Development FEIS [BLM, 1983], lists the types and quantities of solid wastes estimated for the Sand Wash and Paraho-Ute projects [TOSCO, 1982; Paraho, 1982].

Although these projects are quite different in that they employ different retorting technologies, mine different grades of shale at different rates, produce differing amounts and types of final products, and, at times, employ differing control technologies, the rates of solid wastes can be compared when examined on a common basis [Heistand, September 1984]. The common bases used are mined shale (tons of wastes per thousand tons of mined shale, T/MT) and hydrotreated oil (tons of waste per million barrels of oil, T/MMBbl).

TABLE 1.1-1. SFC OIL SHALE PROJECTS

Project	Sponsor	Location	Technology	bbl/day	Federal, $ (millions)	Startup	PSD	NPDES	EIS	EMPO	EMP
				Selected							
Long Ridge Phase I	Union	CO	Union B	10,400	400	In progress	A	A	NA	NA	NA
				Pending							
Phase II	Union	CO	Union C	42,000	2,700	1990	P	P	P	A	
Cathedral Bluffs	Occidental Tenneco Peter Kiewet	CO	Oxy Mis	15,160	2,190	1987	P	A	P[a]	A	
Seep Ridge	Geokinetics	UT	In Situ	1,000	45	1985	P	NA	A	A	
				Proposed							
Ute	Paraho et al.	UT	Paraho	14,105		1987	A	A	A	P	
Means	S. Pacific Petroleum Central Pacific Minerals Dravo	KY	Dravo	13,690		1988			P	P	
Cottonwood Wash	Magic Circle	UT	Paraho	8,547		1988	A	NA	A	P	
American Syn-Crude	American Syn-Crude and Stone & Webster	IN	Petrosix	2,011		1988					

[a] Detailed Development Plan.

Source: Bates, January 1985

KEY

A - Approved
NA - Not applicable
P - Pending approval or modification

TABLE 1.1-2. NON SFC SPONSORED OIL SHALE PROJECTS

Projects	Sponsor	Location	Technology	bbl/day capacity	Startup	PSD	NPDES	EIS
Union Phase II	Union	CO	Union C	90,000 (52,000 SFC)	1994	P	P	P
White River	Sun, Sohio Phillips	UT	Union B Superior TOSCO	100,000	1989	A	P	P[a]
Mobil	Mobil 4 partners	CO	Union B Superior Paraho	100,000	1992		-	A
Pacific	Superior Clev. Cliffs Sohio	CO	Superior TOSCO	100,000	1990		-	A
Getty	Getty	CO	Union Lurgi	100,000	1990		-	A
Cities Service	Cities Service	CO	Union MIS Lurgi	100,000	1991		-	A
Clear Creek	Chevron Conoco	CO	Chevron STB	100,000	1990	P	-	A
Paraho Ute	Paraho et al.	UT	Paraho	42,000 (14,000 SFC)	1988	A	A	A

(continued)

TABLE 1.1-2 (continued)

Projects	Sponsor	Location	Technology	bbl/day capacity	Startup	PSD	NPDES	EIS
Rio Blanco	Standard of Indiana and Gulf	CO	Lurgi	65,000	1988			P[a]
Cathederal Bluffs	Occidental Tenneco	CO	Oxy MIS Union B	117,000 (15,000 SFC)	1987	P	NA	P[a]
Agency Draw	Geokinetics	UT	TOSCO II	23,000	1989		NA	A
Colony	Exxon	CO	Exxon	47,500	1988	P	NA	A
Syntana	Syntana-Utah	UT	Superior TOSCO II	57,000	1994	P	NA	A
Sand Wash	TOSCO	UT	TOSCO II	45,000	(?)	A	NA	A
Midwest Energy	Indiana Shale Oil, Cliffs, Allis Chalmers	IN	Allis Chalmers	50,000	Late 80's			
Cottonwood Wash	Magic Circle	UT	Paraho	31,500 (13,547 SFC)	1988	A	NA	A

[a] Detailed Development Plan.
Source: Bates, January 1985

KEY

A - Approved
NA - not applicable
P - pending approval or modification

Factors were determined on the basis of shale mined and oil produced for sixteen solid wastes, grouped into two categories, as shown in Table 1.1-3 [Heistand, September 1984].

Using the factors presented in Table 1.1-3, it is possible to calculate probable rates of various solid wastes produced based upon projected mining rates and product oil production for the above-ground oil shale retorting facilities.

A surface retorting plant, such as a TOSCO II processing facility, will be a source of large quanitities of plant wastes which will require disposal. Table 1.1-4 indicates the makeup of the waste material that will be discarded from a small TOSCO II plant over a period of 20 years.

1.2 POTENTIAL DANGERS TO HUMAN HEALTH AND THE ENVIRONMENT FROM THE DISPOSAL AND REUSE OF THE WASTES

Although oil shale facilities will produce huge volumes of solid wastes, the potential for reuse of the wastes is small. Some wastes such as spent catalysts could potentially be reclaimed and recycled back into the process. Elemental sulfur, removed by some air pollution control technologies, has a limited market potential; however it remains to be demonstrated on a commercial scale that there are no trace impurities that would constrain its use. It is expected that hazardous wastes such as spent catalysts and some sludges will be disposed in licensed hazardous waste facilities. However, one catalyst unique to shale oil upgrading is of particular concern. The arsenic guard bed catalyst will contain 20% or more arsenic. No facilities exist to reprocess this spent catalyst and environmentally safe disposal may be difficult to achieve. Other than the arsenic guard bed catalyst, the major unique dangers to health or the environment posed by oil shale facilities may be from the long term effects of on site disposal of millions of tons of retorted oil shale, raw oil shale waste, and other process wastes. Principal concerns in this regard may be summarized as follows:

1. Auto oxidation/auto ignition may be a serious problem if disposal of raw shale fines and/or carbonaceous spent shales are not done in a manner to minimize this risk.

2. High inorganic salt loading and possibly organics in leachates from raw shale fines or spent shale could potentially have significant impacts on groundwater supplies in the area and on surface waters that supply millions of people (Colorado River). A related issue is to what extent should process wastewaters be treated prior to codisposal with the retorted shale. Codisposal of spent catalysts and treatment sludges may also significantly impact the nature of leachates from disposal sites.

TABLE 1.1-3. APPROXIMATE SOLID WASTE RELATIONSHIPS[a]

Type of waste	Mined shale basis, T/MT	Hydrotreated oil basis, T/MMBbl
Major	834.5	
Retorted shale	784.4	
Raw fines, dust, subore	58.8	
Off-spec sulfur	1.3	
Oily particles[b]	0.49	
WWT sludge[b]	0.14	
Scrap and garbage	0.10	
Catalysts and other wastes		27.76
Methanator		0.48
Reformer		1.10
Hydrotreater (HDN, HDS)		17.22
Lo-temp CO shift		2.29
Alumina		5.04
DEA sludge		0.95
API sep. btms.		24.44
API float		2.12
Hi-temp CO shift (FeCr)		1.26
Arsenic guard bed		36.31

[a] These factors will give values which may range +100% to -50%.

[b] Based on solids content.

Source: Heistand, September 1984.

3. Infiltration of moisture into disposal sites from precipitation or from surface or groundwater intrusion could lead to sudden pile failure. Such failure could cause extensive property damage, threaten lives, and contaminate the drinking water supply for millions of people.

Auto-Oxidation/Auto-Ignition

Auto oxidation leading to auto ignition of some coals and coal wastes has been known to be a problem for many years. Some coal wastes piles in the east are believed to have ignited in this manner while the phenomenon is fairly common with western lignite coals. Since raw oil shales and some retorted oil shales possess carbonaceous material and are capable of being ignited, EPA has recently conducted several tests to assess the potential for auto-ignition of raw oil shale fines and retorted oil shales. The results indicate that raw shale fines have a potential similar to bituminous coals while retorted shales appear to be less reactive (Table 1.2-1). Hence there is a potential that if oil shale

TABLE 1.1-4. MAJOR WASTE PRODUCED OVER A PERIOD OF 20 YEARS (TOSCO II 47,000 bbl/day plant with upgrading)

Stream description	Quantity, 10^6 tons	Material quantity as a percent of total waste quantity
Raw shale runoff and leachate	N.D.[a]	N.D.
Raw shale sludge - preheat system	11.31	2.27
Processed shale sludge - ball elutriator	0.85	0.17
Processed shale sludge - moisturizer	0.57	0.11
Processed shale	350.84	70.43
Stripped foul water	18.49	3.71
Compression condensate - Wellman-Lord Unit	1.73	0.35
Coke[b]	5.26	1.06
Stripped sour water purge stream	0.75	0.15
Revegetation water	14.59	2.93
Dust suppression water	9.70	1.95
Boiler blowdown	11.04	2.22
Boiler feedwater treatment concentrate	4.81	0.97
Cooling tower blowdown	60.31	12.11
Storm runoff	4.34	0.87
Processed shale leachate	N.D.	N.D.
Spent catalysts	0.005	0.001
Treated sanitary water	0.55	0.11
Sanitary water treatment sludge	N.D.	N.D.
Service and fire water runoff	0.63	0.13
Source water clarifier sludge	2.37	0.48
Trash, construction debris, etc.	N.D.	N.D.
TOTAL	498.15	99.93

[a] N.D. - Not determined.

[b] Most of the coke can be sold as a by-product.

Source: EPA 600/8-83-003, April 1983

disposal sites are not properly designed they could auto-ignite producing huge quanities of pollutants such as SO_2, NO_x, H_2S, CO_2 and hydrocarbons. Such combustion could impair pile stability leading to failure of the disposal pile and/or substantially accelerate the leaching process. Since oil shale disposal sites will occupy several square miles and be hundreds of feet thick, there is no known method for extinguishing combustion should it get started. Hence, the key to controlling ignition must be the design and incorporation of appropriate controls when the disposal site is constructed. It appears probably that control technology employed by the coal industry can be modified and applied to oil shale disposal sites to mitigate this hazard.

TABLE 1.2-1. SUMMARY OF RESULTS FROM DIFFERENTIAL
DIFFERENTIAL SCANNING CALORIMETRY[a] AND
NONADIABATIC OXYGEN ABSORPTION[b] TESTING

	DSC[c]		
Materal	Onset, °C	Exotherm, J/g	Nonadiabatic test S index
Wyoming Subbituminous Coal	190	10,900	165
Western Kentucky #9 Bituminous Coal	193	13,800	60
Utah Raw Shale (66 GPT)	211	8,320	86
C-a Raw Shale	226	920	5.6
Utah Raw Shale (28 GPT)	227	2,990	44
Pocahontas #3 Bituminous Coal	230	15,700	42
Paraho Retorted Shale	300	480	0.27
TOSCO II Retorted Shale	306	560	1.4
Union Shale Mixture	321	860	4.6
Hytort Retorted Shale	357	1,340	3.8
Lurgi Retorted Shale	-[d]	~0	0.00

[a] Lower onset temperature means more reactive.

[b] Higher S index means more reactive.

[c] Test in dry air, particle size: -325 mesh.

[d] No exotherm observed to 550°C.
Source: EPA 600/2-84-153, 1984.

Leaching

The composition of retorted oil shales vary principally in response to the properties of the raw shale feed and the retorting process. The composition of any leachates from retorted shale disposal sites will vary depending upon the properties of the retorted shale, and other wastes codiposed with the retorted shale, such as wastewaters for cooling/wetting and treatment sludges. Anticipated composition for Union B retorted shale is provided in Table 1.2-2, process water for cooling and wetting the shale in Table 1.2-3, and properties of Unisulf solution, Unisulf sulfur byproduct, and moistened retorted shale are provided in Table 1.2-4. Some leaching test results on Union B retorted shale are

TABLE 1.2-2. CHEMICAL PROPERTIES OF UNION B RETORTED SHALE

Components[a]	Weight, %
Major elements as oxides	
SiO_2	31.5
CaO	19.6
MgO	5.7
Al_2O_3	6.9
Fe_2O	2.8
Na_2O	2.2
K_2O	1.6
SO_3	1.9
P_2O_5	0.4
Other properties	
Mineral CO^2	22.9
Organic C	4.3
Nitrogen, Kjeldahl	0.2
Free silica (quartz)	8.0
pH of slurry	8.7

[a] Analyses determined by heating sample to 950°C for pH measurement. Analyses by Union Research Department.
Source: Battelle PNL 3830, 1981

TABLE 1.2-3. ESTIMATED[a] COMPOSITION OF PROCESS WATER FOR RETORTED SHALE COOLING/WETTING

Parameter	Reuse water sump, mg/L
Alkalinity (as $CaCO_3$)	2,000
Carbonate (as CO_3)	400
Bicarbonate (as HCO_3)	1,700
Chemical oxygen demand	5,500
Total organic carbon	1,350
Total dissolved solids	2,600
Total solids	3,100
Hardness (as $CaCO_3$)	900
Ammonia	35
Sulfides (as H_2S)	100
Phenols	125
Cyanide (CN)	20
Oil and grease	1,300
Sulfate	500
Sodium	1,500
Arsenic	6.5
Chromium	0.5
pH units	8-10

[a] These values are maximum design case levels based on preliminary bench-scale tests and engineering calculations. Source: Union Oil Company, January 1984.

TABLE 1.2-4. RCRA TESTING OF SIMULATED SHALE PLANT WASTES (UNION B PROCESS)

	Unisulf sulfur	Moistened retorted shale plus fines[a]	Maximum allowed	Minimum allowed
Ignitability				
Causes fire through friction	No	No	-	-
Oxidation	0°F	0°F	-	-
Corrosivity				
a) pH	-	-	12.5	2.0
b) Steel corrosion (in/yr)	-	-	0.25	-
Reactivity				
Yield gases, vapors or flames when exposed to water	No	No		
Yields H_2S or HCN when exposed to pH 2 buffer	No	No		
Reacts explosively				
a) When subjected to burner flame	No	No		
b) When under heated confinement	No	No		
EP Toxicity, mg/L				
Arsenic	<0.01	0.07	5.0	
Barium	0.2	<2.7	100.0	
Cadmium	<0.01	<0.01	1.0	
Lead	<0.05	<0.05	5.0	
Mercury	0.002	<0.0005	0.2	
Selenium	<0.0005	<0.0005	1.0	
Silver	<0.02	<0.02	5.0	

[a] Moistened with simulated process water.

Source: Union Oil Company, January 1984.

TABLE 1.2-5. CHEMICAL COMPOSITION OF LEACHATES FROM UNION B RETORTED SHALE (mg/L)

Compound	Union Oil Company 1982c	Stearns-Rogers 1976	Cleave et al. 1979	Woodward-Clyde 1975
Ag	-	-	<0.009	<0.009
Al	<0.3 - 0.12	-	-	<0.05 - 0.27
As	0.005 - 0.022	0.066	<0.001	-
B	0.22 - 17.0	8	0.97	-
Ba	0.09 - 0.11	0.03	<0.078	-
Be	<0.05	-	-	-
Ca	46 - 460	17	243	69 - 424
Cd	<0.01 - 0.03	<0.02	0.016	-
Cl	7 - 120	210	7.0	8 - 91
CN	0.003 - 0.009	<0.005	-	-
Co	<0.03 - 0.05	-	-	-
Cr	0.003 - 0.012	0.01	<0.011	-
Cu	<0.02 - 0.2	-	<0.011	-
F	5.6 - 11.4	-	-	-
Fe	<0.5 - 6.5	-	<0.025	<0.05 - 20
HCO_3	92 - 257	2,370	172	4 - 32
Hg	<0.0005 - 0.001	-	-	-
K	4.6 - 48	14	7.4	3 - 85
Li	0.1 - 0.6	-	-	-
Mg	29 - 1,400	50	58	5 - 55
Mn	0.2 - 6.7	-	<0.007	-
Mo	0.8 - 4.0	27	-	-
Na	11 - 4,800	5,040	109	45 - 750
Ni	<0.02 - 0.12	-	-	-
NH_3-N	<1 - 4	2.4	-	-
NO_3-N	<10 - 100	2.0	-	2 - 5
Oil and grease	<2 - 5	25	-	31 - 111
Pb	0.05 - 0.5	<0.2	0.009	-
Phenols	<0.001 - 0.0086	<0.005	-	-
PO_4	<200	-	-	-
Se	<0.005 - 0.018	-	<0.001	-
Si	1 - 4	-	-	0.5 - 4
SO_4	115 - 19,100	7,090	878	230 - 2,400
Sr	1.1 - 7.6	-	-	-
TDS	327 - 25,000	16,000	1.518	410 - 4,860
TOC	0 - 31	240	11.3	-
Zn	0.04 - 0.26	-	0.025	-
pH, units	7.5 - 7.9	7.6	8.33	3.1 - 6.9

Source: Union Oil Company, January 1984.

TABLE 1.2-6. RETORTED SHALE LEACHATES BY LEACHING METHOD (mg/L)

Shale	Parameter pore volume	Field	RCRA	ASTM	Column initial	Column[a]
Paraho	pH	9.57	9.27	12.05	11.55	12.35
	Ec (µS/cm at 25°C)	21.100	4,600	2,800	9,230	6,250
	HCO_3	-	2,723	5	15.3	4.8
	CO_3	-	217	236	232	463
	SO_4	12,350	226	536	3,840	2,045
	Cl	526	29	7	49	14
	F	11.9	-	13.5	21	11.4
	Mg	7.7	484	0.5	1.6	1.7
	Na	5,591	37	145	1,500	285
	Ca	421	724	266	610	670
	K	834	6.5	31	140	38
TOSCO II	pH	8.9	7.72	8.69	9.24	9.21
	Ec (µS/cm at 25°C)	10,000	5,710	2,650	35,080	5,180
	HCO_3	-	3,325	191	619	188
	CO_3	-	-	-	46	13
	SO_4	30,270	229	1,130	25,000	2,470
	Cl	-	22	10	178	13
	F	13	-	20.2	27	29.5
	Mg	156	81	35	628	60
	Na	10,270	131	545	10,095	945
	Ca	463	1,872	31	545	83
	K	110	3.9	8	89	11
Lurgi[b]	pH	-	8.67	11.85	12.24	11.93
	Ec (µS/cm at 25°C)	-	5,650	4,270	59,500	4,250
	HCO_3	-	2,940	6.9	10.5	7
	CO_3	-	59	210	775	203
	SO_4	-	880	2,290	34,000	2,070
	Cl	-	19	17	2,250	15
	F	-	-	6.3	26.4	7.6
	Mg	-	430	0.4	3.5	0.3
	Na	-	55	275	18,770	325
	Ca	-	1,479	713	535	575
	K	-	11	64	1,464	150

[a] Paraho - 0.198; TOSCO II - 1.03; Lurgi - 0.621.

[b] Several Lurgi shales have been tested and results differ slightly. Example provided is Lurgi shale provided by Rio Blanco Oil Shale.

Source: EPA-600/D-84-036, March 1984.

TABLE 1.2-7. RAW MINED OIL SHALES LEACHATES (MAXIMUM OBSERVED CONCENTRATIONS)

Species	Concentration, mg/L	Location[a]	Date
HCO_3	579	C-a, 15 ft	9/21/82
CO_3	5.68	C-a, 15 ft	7/19/82
TDS	72,660	C-a, 15 ft	8/16/82
F	113	C-a, 15 ft	7/26/82
Cl	366	C-a, 15 ft	7/01/82
PO_4	0.28	C-b, 20 ft	2/25/82
NO_3	2,564	C-a, 15 ft	7/26/82
SO_4	45,900	C-a, 15 ft	5/10/82
Zn	0.597	C-a, 15 ft	8/16/82
Fe	2.02	C-a, 15 ft	8/11/82
Co	1.17	C-a, 15 ft	8/23/82
Li	0.339	C-b, 10 ft	7/26/82
NH_3	2.55	C-a, 5 ft	8/30/82
B	1.97	C-b, 15 ft	7/26/82
Cd	0.168	C-a, 15 ft	7/26/82
Be	0.300	C-b, 10 ft	7/06/82
Mg	12,830	C-a, 15 ft	9/06/82
P	7.0	C-a, 15 ft	8/04/82
Si	13.2	C-a, 15 ft	6/02/82
Mo	1.5	C-b, 10 ft	7/06/82
Mn	2.34	C-a, 15 ft	6/02/82
Ni	1.12	C-a, 15 ft	6/02/82
Na	2,030	C-a, 15 ft	8/02/82
Cu	0.073	C-b, 10 ft	7/06/82
Al	5.28	C-a, 5 ft	7/01/82
Ca	505	C-a, 15 ft	3/22/82
Ba	0.822	C-b, 10 ft	9/23/82
K	16.4	C-a, 15 ft	7/19/82
Cr	0.290	C-a, 15 ft	6/02/82
Sr	15.4	C-a, 15 ft	7/19/82
Pb	1.036	C-a, 15 ft	8/11/82
Ag	0.012	C-a, 15 ft	3/17/82
Tℓ	0.007	C-a, 15 ft	4/12/82
Se	0.013	C-a, 15 ft	7/01/82
As	0.007	C-b, 20 ft	8/04/82
Hg	0.003	C-b, 20 ft	2/25/82

[a] 5, 10, 15, and 20 foot deep Lysimeters on Federal lease tracts Ca and Cb.

Source: EPA-600/D-84-228, 1984.

provided in Table 1.2-5 while results on several other retorted shales (all without codisposed wastes) are presented in Table 1.2-6. Some raw mined oil shales have been leached under field conditions and the results are in Table 1.2-7.

A significant volume of data such as that above exists. This data indicates that even if raw and retorted shale wastes are not defined as hazardous, the leachates from these wastes are high in dissolved salts as well as other contaminents and could seriously impact surface or groundwater supplies, provided significant amounts of leachate are produced. The amount of leachate produced will depend to large extent on site specific characteristics and the disposal controls employed. Since billions of tons of retorted oil shale may eventially be produced, the cummulative impact on water quality could be very great. Table 1.2-8 indicates the quantity of some constituents leachable from oil shale wastes. As previously discussed a 600,000 bbl/day oil shale industry would produce about 270 million tons/per year of retorted shale, which would accumulate to nearly 8 billion tons after 30 years of operation. Such a quantity of waste will possess the potential for leaching hugh quanitities of contaminents. For example assuming 8 billion tons of TOSCO II retorted shale, then 58 million tons of sulfate are leachable along with 100 million tons of total dissolved solids and lessor amounts of many other contaminents. The key to preventing serious environmental impact does not lie in preventing the leaching (since erosion of the disposal sites and leaching will eventually occur) but rather in employing controls to assure that the rate of release of contaminents is slow enough to be accomodated without substantial environmental damage. These controls must be designed and built into the disposal sites from the beginning since the huge size of the disposal sites will make any retrofit operations extremely expensive and likely impossible.

Mass Failure

Retorted oil shale disposal sites will be the largest solid waste disposal sites ever constructed. A typical 50,000 bbl/day surface retorting plant will produce about 450 million cubic feet/year of solid waste, which over an operating plant life of 30 years would cover an area of about 3.5 square miles to a depth of 150 feet. [EPA 600/2-80-205a, 1980]. Most disposals will be head of hollow or cross canyon fills, miles in length and hundreds of feet deep. Mass failure of one of these fills could have major impacts causing extensive property damage and threatening lives. Failure of one of several disposal piles proposed could destroy downstream reservoirs, shale oil upgrading, storage, and loading facilities, and deposit millions of tons of leachable retorted shale in the Colorado River.

The most likely cause of a disposal pile failure would be saturation of the waste pile and/or liquefaction of the pile bottom leading to slippage. Moisture contributing to this problem could

TABLE 1.2-8. ESTIMATED QUANTITIES OF SOME MAJOR CONSTITUENTS LEACHABLE FROM OIL SHALE (ASSUMING PERMEABILITY AND WATER AVAILABILITY ARE NOT LIMITING FACTORS)

Characteristic	Raw shale	TOSCO	USBM	Union A	Simulated in-situ
Constituent (kg leached/tonne shale):					
Ca^{++}	0.1	1.14	0.42	3.27	0.04 - 2.1
Cl^{-}	0.02	0.08	0.42	0.33	0.06
HCO_3^{-}	0.75	0.20	0.38	0.28	0.22 - 0.40
K^{+}	0.24	0.32	0.72	6.25	0.000 - 0.18
Mg^{++}	0.01	0.27	0.04	0.91	0.00002 - 0.08
Na^{+}	0.48	1.65	2.25	21	0.09 - 2.35
SO_4^{--}	0.79	7.3	6.00	62	0.50 - 1.3
TDS (103°C)	2.77	12.6	10.9	100	-
pH	8.15	8.40	7.78	9.94	7.76 - 12.7
Conductance (μmhos at 25°C)	310	1750	1495	11,050	-

Source: EPA 600/2-80-205a, 1980.

come from codisposed wastewaters, precipitation and infiltration, groundwater intrusion into the pile, or surface streams routed over or through the disposal site. The principal approach to prevent these problems is therefore to control the movement of moisture into or through the disposal pile. To accomplish this requires the incorporation of a number of control technologies into a complex site and material specific design. Although the basic technologies to be employed are well known (i.e., drains, liners, covers, earth fill dams, benching) their construction on the scale required and application to oil shale wastes have never been demonstrated.

1.3 PRESENT/PROPOSED DISPOSAL APPROACHES

Due to the high volumes of solid wastes produced by an oil shale facility, the environmentally safe disposal of these wastes must be engineered on a site and process specific basis. The slate of solid wastes to be disposed and their chemical nature will vary in response to the nature of the raw shale feed, the particular retorting process employed, the specific plant design including pollution control technologies, and whether raw shale oil is upgraded on site. The design of the solid waste disposal site as well as the selection and application of appropriate control technologies must be tailored to accomodate not only the quantities and nature of the wastes but also the characteristics of the specific disposal site. Alternative disposal practices and control technologies are generally well known. All have been proposed or considered by one developer or another though no developer has yet proposed a plan incorporating all the control features that might be desired into a specific design for solid waste disposal.

Disposal Approaches

The following discussion applies to the basic methods for handling solid wastes produced by a surface retorting process. The key features of each approach are summarized in Table 1.3-1. A discussion of the control technologies applicable to these disposal alternatives is presented.

Landfills

A landfill basically entails placing the waste material as a compacted fill in a suitable location. The wastes from the processing facility are transported to the disposal site by conveyors or trucks and then hauled to the active portion of the landfill. Preferably, the solid wastes are then laid down in lifts of 9-18 inches and compacted to a suitable in-place density. The compacted fill may be built with a proper slope to a vertical height of 40-50 feet and then flattened, or benched, to provide a passageway for the disposal equipment and to facilitate runoff collection. The overall landfill can be constructed gradually in this fashion, using a multiple-bench arrangement.

TABLE 1.3-1. KEY FEATURES OF SOLID WASTE DISPOSAL APPROACHES

Disposal approach	Principle	Advantages	Disadvantages
Landfills	Place wastes as fill in a convenient surface location and isolate from the surrounding environment.	Relatively simple placement and isolation of wastes. Does not interfere with production.	Dust and erosion control and reclamation/revegetation are relatively labor-intensive operations. Occupies a significant amount of land surface.
Underground mine backfill	Place wastes as fill in the inactive parts of the mine.	Decreases subsidence and size of necessary surface landfill. No additional maintenance or reclamation work is required. May enhance total resource recovery.	Difficult to isolate the wastes from the surrounding environment. Placement is relatively difficult, complex, and interferes with production.

Source: EPA 600/8-83-003, April 1983.

Depending upon the geography of the disposal site, the landfill may be built on a level or nearly level surface, in the head of a valley, or across a valley. The applicable control technologies will vary somewhat with site topography but still will be designed to protect the surface and subsurface waters. Applicable control technologies include runon and runoff catchment ponds, embankments and diversion systems, liners and cover, and revegetation. Provision for structural stability of the fill is also a major consideration.

A surface landfill of some type will need to be included in most oil shale developments. This results from the shale undergoing a volume expansion upon mining, crushing, and processing, which precludes all of the shale being returned to the mine.

Underground Mine Backfill

In this disposal approach, the waste material is placed in the inactive portion of the underground mine (e.g., a room-and-pillar mine), while production continues in other parts of the mine. This approach is attractive from several viewpoints. By returning the wastes to the mine, the size of a surface landfill would be greatly reduced. The potential for mine subsidence would be diminished. Backfilling the mine may enhance resource recovery by increasing the amount of shale that can be mined safely. Disadvantages include possible release of volatiles underground in the workplace and possible groundwater contamination.

The major considerations in backfilling involve developing logistics for carrying out simultaneous mining and disposal operations while providing protection for workers and the groundwater. For fine processed shales, like the TOSCO II, hydraulic or slurry backfilling may be practical. However, additional water, above the moistening needs, would be required and a drainage collection system would be needed. The wastes may be transported to the mine by conveyors or trucks, then compacted in place, but the space limitations reduce the practicability of this approach. Alternatively, the wastes may be backfilled pneumatically, but this approach may be difficult to implement at the scale required.

A study on the above backfilling techniques has been conducted for the wastes from the Colony project [Dravo Corp., 1975]. The results indicate that, while theoretically 80% of the wastes could be returned to the mine, only 60% of the wastes can actually be placed in the mine during the project life due to a time lag of 5-10 years between the mining and backfilling operations. It was concluded that none of the placement techniques were developed sufficiently to be applied on a large scale.

Impacts of Disposal Alternatives on the Use of Oil Shale and Other Natural Resources

Due to the huge volume of solid wastes, especially retorted shale, produced by an oil shale facility, these wastes must be disposed on or close to the plant site. In the case of open pit mines, such as the one proposed for federal lease tract Ca, huge amounts of overburden and subgrade oil shale will also require disposal. These wastes could be disposed entirely on the surface as piles or canyon fills or could partially be returned to the mine. Either way the leaching potential of these wastes must be carefully controlled or leachates will seriously impair the quality and use of surface and groundwater supplies. Depending upon the specific placement of these wastes they could also impair future access to other oil shale resources. Returning some of the retorted oil shale to an underground mine would be expensive and technically difficult but could actually increase the potential for resource recovery by facilitating mining of the support pillars.

Potential Utilization of Oil Shale Solid Waste

Oil shale solid wastes having some potential for utilization include retorted oil shale, raw shale fines, spent catalysts, elemental sulfur and biological treatment sludges. Retorted oil shales, particularly decarbonized shales, have some limited potential for utilization on site. Decarbonized western oil shales posses a significant capacity to cement similar to low grade commercial cement. Hence a very limited amount of retorted shale may be used locally as a low grade cement substitute. Raw shale rejects and fines, from mining and raw shale preparation, could be processed in specially designed retorts or possibly formed into bricketts and processed in the regular plant facilities. Spent catalysts could potentially be reclaimed and reused in the upgrading process, though facilities to reclaim them do not presently exist. Some air pollution control technologies remove elemental sulfur which, if not contaminated by impurities, should have at least a limited market for agricultural use. Biological treatment sludges may be useful on site as soil conditioners for revegetation if they do not contain significant quantities of harmful contaminents. However, even if all the above wastes are utilized to the maximum extent possible, it will not make a significant impact on the amount of solid waste to be disposed.

1.4 CONCLUSIONS AND ADDITIONAL RESEARCH NEEDED

Conclusions

1. The oil shale industry will produce unprecedented volumes of solid waste mostly consisting of retorted oil shales, raw oil shale fines, overburden and subgrade ore, codisposed wastewater, and much smaller quantities of known hazardous wastes. Although the known hazardous wastes will be sent to licensed disposal or recycling facilities, the high volume solid wastes will be disposed on or close to the plant site. If not properly managed these high volume wastes are capable of producing leachates that could contaminate the water supply for millions of people. Some of the waste may also pose the hazard of auto ignition unless proper controls are employed. Surface disposal sites covering square miles in area and hundreds of feet in thickness would do extensive property damage and threaten lives should they ever suffer sudden mass failure.

2. Control technologies to prevent serious adverse impacts from disposal of billion of tons of oil shale wastes have been proposed but their application to oil shale waste materials and on the scale required has not been demonstrated. Further, to be effective, these technologies, must be applied in highly technical and integrated disposal designs that are site and process specific. There is no current experience in disposal of wastes of similar composition or of volumes approaching that which will result from the oil shale industry.

Additional Research Needed

a. Solid wastes (including codisposed wastewaters) from oil shale facilities need to be characterized.

b. The effects from codisposal of liquid and solid wastes need to be determined. Related question is to what extent should wastewater be treated prior to codisposal with retorted shale.

c. Effective means of controlling moisture movement into and from retorted shale disposal site to achieve mass stability and minimize leachate need to be developed and demonstrated. Included are liners and covers made from retorted shale, drains installed above and below liners, use of vegetation to reduce infiltration, and means of relocating surface drainage in filled canyons.

d. The nature and quantity of leachate produced from disposal sites employing state-of-the-art technology needs to be determined.

e. A best management practices design manual needs to be developed to guide developers and permitters in the selection of appropriate control technologies and the integration of these technologies into complex site and process specific disposal designs.

SECTION 2

CHARACTERISTICS OF U.S. OIL SHALE

2.1 INTRODUCTION

This section describes the location, geology, composition, and the physicochemical properties of oil shale resources in the United States.

Oil shale is commonly defined as a fine-grained sedimentary rock containing organic matter (known as kerogen) that is essentially insoluble in petroleum solvents, but that yields substantial quantities of liquid oil, gases, and residual carbon upon pyrolysis [Culbertson et al., 1973].

2.2 LOCATION

The principal United States oil shale deposits are presented in Figure 2.2-1 [Duncan et al., 1965]. These deposits occur in four general locations; (a) the Tertiary period (Eocene) deposits of the Green River Formation in Colorado, Utah, and Wyoming; (b) the late Devonian and early Mississippian period marine shales of the central and eastern United States, stretching from Michigan and Pennsylvania southward through Indiana and Kentucky to Texas; (c) the early Cretaceous and upper Triassic marine shales in Alaska; and (d) the small Tertiary shale deposits of Montana, Nevada, Idaho, and California [EPA-600/2-80-205a, 1980].

It has been estimated that an equivalent of seven trillion barrels (bbl) of oil are contained in the U.S. reserves of shale oil, but not all of these deposits are sufficiently rich in organic matter to be considered commercially attractive. Estimates place total known U.S. oil shale resources for oil shales yielding 10 gal of oil per ton of shale at well over 2 trillion bbl [Duncan et al., 1965]. The Green River Formation oil shales in Colorado, Utah, and Wyoming account for an estimated 90 percent of this total resource and are therefore regarded as being the most important commercially.

The Devonian Marine black shales of the central and eastern United States are estimated to contain at least 400 billion bbl of equivalent oil. While they have not received as much commercial interest as the Green River Shales, there are commercial projects proposed

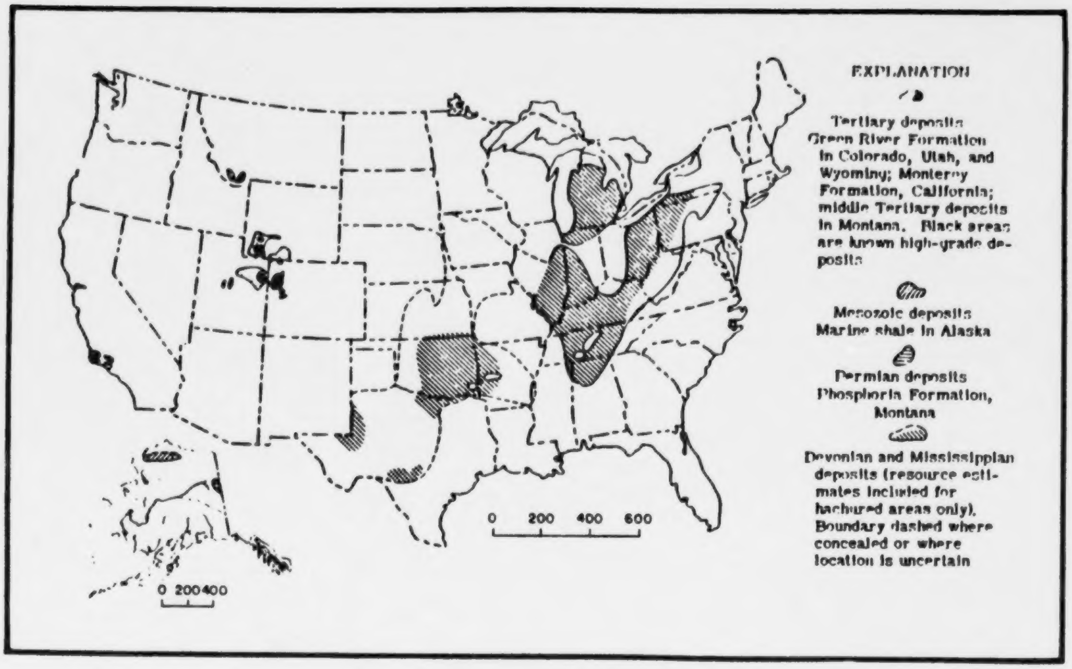

EXPLANATION
Tertiary deposits Green River Formation in Colorado, Utah, and Wyoming; Monterey Formation, California; middle Tertiary deposits in Montana. Black areas are known high-grade deposits
Mesozoic deposits Marine shale in Alaska
Permian deposits Phosphoria Formation, Montana
Devonian and Mississippian deposits (resource estimates included for hachured areas only). Boundary dashed where concealed or where location is uncertain
0 200 400 600
0 200 400

Figure 2.2-1. Principal United States Oil Shale Deposits. Source: Duncan et al., 1965

for their development. The Institute of Gas Technology has demonstrated that retorting in the presence of hydrogen (hydroretorting) can increase the oil yield of the Eastern Devonian Shales, by a factor of 2.5 [Tarman et al., 1967]. The Alaskan marine shales and the Tertiary shales of California and elsewhere have received little attention to date and are not considered to be commercially attractive.

2.2.1 Green River Formation Oil Shale

As shown in Figure 2.2-2, the oil shale deposits of the Green River Formation occur in a 16,988 mi^2 area in northwestern Colorado, northeastern Utah, and southwestern Wyoming. The richer oil shales, those of highest commercial interest, are generally more centrally located in the four depositional basins: Piceance Creek basin, Colorado; Uinta basin, Utah; and the Green River and Washakie basins of Wyoming. The Piceance Creek basin of Colorado contains the thickest and richest oil shale deposits within the United States, and accordingly, the greatest interest related to commercial development has been directed to that area.

Table 2.2-1 presents the total in-place shale oil resources of the Green River Formation. Total identified shale oil resources in place, which average 15 gal/ton or more in strata up to 2,000 ft thick, are estimated to be 179 billion tons in Colorado's Piceance

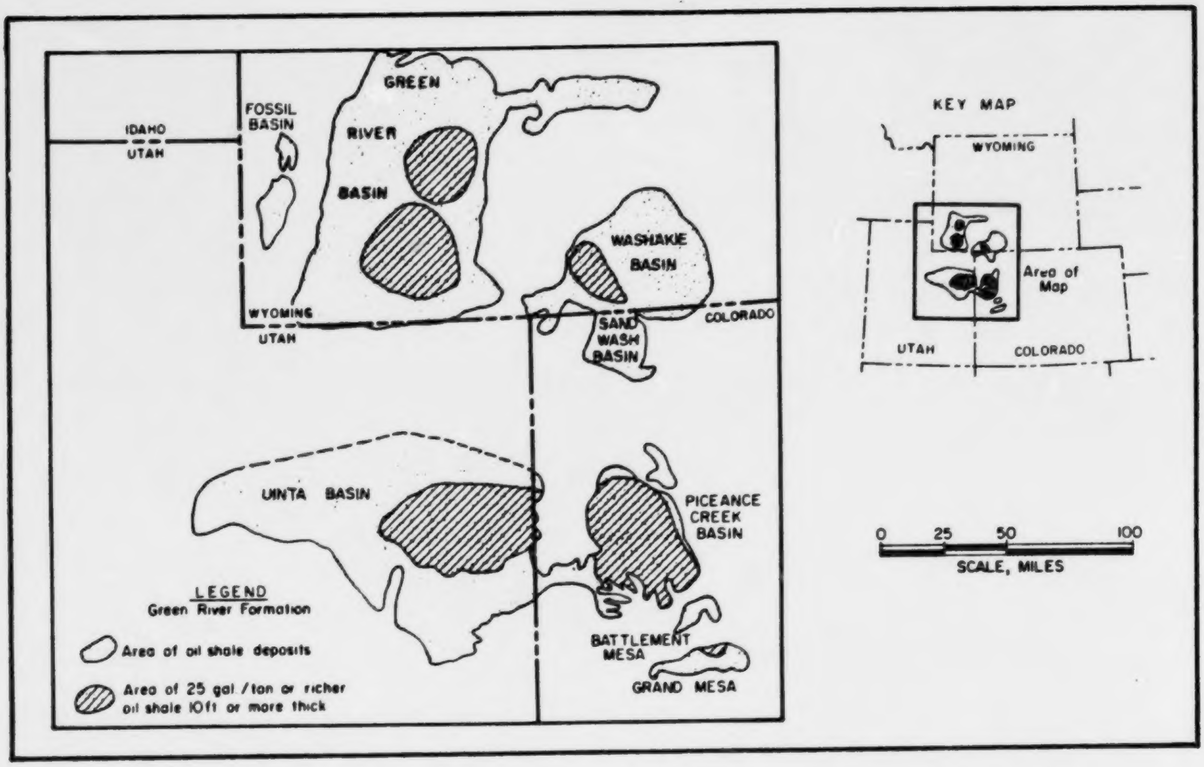

GREEN RIVER BASIN
FOSSIL BASIN
IDAHO
UTAH
WYOMING
UTAH
WASHAKIE BASIN
COLORADO
SAND WASH BASIN
UINTA BASIN
PICEANCE CREEK BASIN
BATTLEMENT MESA
GRAND MESA
LEGEND
Green River Formation
Area of oil shale deposits
Area of 25 gal/ton or richer oil shale 10 ft or more thick
KEY MAP
WYOMING
Area of Map
UTAH
COLORADO
0 25 50 100
SCALE, MILES

Figure 2.2-2. Green River Formation Oil Shales-Utah, Colorado, and Wyoming. Source: Baughman, 1978 (Reproduced with permission.)

TABLE 2.2-1. TOTAL IN-PLACE SHALE OIL RESOURCES OF THE GREEN RIVER FORMATION[a]

	Type of shale (yield/tonne)					
	62.6 L/tonne (15 gal/ton) or more		104.3 L/tonne (25 gal/ton) or more		125.2 L/tonne (30 gal/ton) or more	
Location	Billions of tonnes	Billions of equivalent barrels of oil	Billions of tonnes	Billions of equivalent barrels of oil	Billions of tonnes	Billions of equivalent barrles of oil
Colorado	163.2	1,200	82.6	607	48.3	355
Utah	43.7	321	8.7	64	6.8	50
Wyoming	43.7	321	8.2	60	1.8	13
TOTAL	250.6	1,842	99.5	731	56.9	418

[a] In beds at least 10 ft thick.

Source: Ash, 1964.

Creek Basin, 48 billion tons in Utah's Uinta Basin, and 48 billion tons in the combined Green River, Washakie, and Sand Wash basins of Wyoming. The three-state total is thus 1,842 billion bbl. The total in-place resource is not presently recoverable, but it is estimated by the U.S. Geological Survey (USGS) that approximately 80 percent of the known shale that yields 25 gal/ton or more, or some 88 billion tons of shale oil are suitably located and of adequate thickness to be reasonably regarded as the potentially recoverable resource base. If 50 percent of the 25 gal/ton or more resource could be recovered, it would be large enough to produce 2 million bbl/day, or over one-fourth the present daily imports, for more than 400 years. Table 2.2-1 shows that 80 to 85 percent of the in-place, 25- to 30-gal/ton oil shale resource are in Colorado's Piceance Creek Basin, with the remainder divided between Utah's Uinta Basin and Wyoming.

2.2.2 Devonian-Mississippian Black Shales

The black marine shales of the Devonian/Mississippian periods are located in the Eastern and Central States. These shales, part of an original shallow inland sea, occur over an area of more than 400,000 mi^2 in Ohio, Kentucky, Tennessee, Indiana, Michigan, Alabama, and extend as far southwest as Oklahoma and Texas. As shown in Figure 2.2-3 black shale deposits also occur in the northern great plains and extend into Canada.

The Devonian shales are lean by western shale standards, with an average Fisher assay of only 10 gal/ton; however, the carbon content of Devonian shales is typically about 14 percent, or approximately the same as Green River shale assaying 30 gal/ton. The difference in Fischer assay is due to the higher carbon to available hydrogen weight ratio of the 10 gal/ton Devonian shale (11.2 to 1) as compared with the 30 gal/ton Green River shale (7.2 to 1). If, however, the 10 gal/ton Devonian shale is retorted in the presence of hydrogen (i.e., hydroretorted), oil yield can be increased to 25 gal/ton, according to research conducted by the Institute of Gas Technology (IGT) [Tarman et al., 1977].

The higher oil yields possible with hydroretorting can, of course, have an influence on defining the Devonian shale resource base. The USGS estimate of equivalent oil in place in Devonian shales is 400 billion bbl, without considering the effect of hydrogen in retorting. With hydroretorting, this value could easily increase to 1 trillion bbl, or 250 percent of the conventional Fischer assay.

The Institute of Gas Technology has surveyed the three-principal Devonian shale basins (Appalachian, Illinois, and Michigan) and estimated that some 423 billion bbl of oil could be recovered from the 6,200 mi^2 of outcrops and relatively shallow deposits in these basins alone if hydroretorting were employed. Their criteria for a recoverable resource required that a shale deposit have an

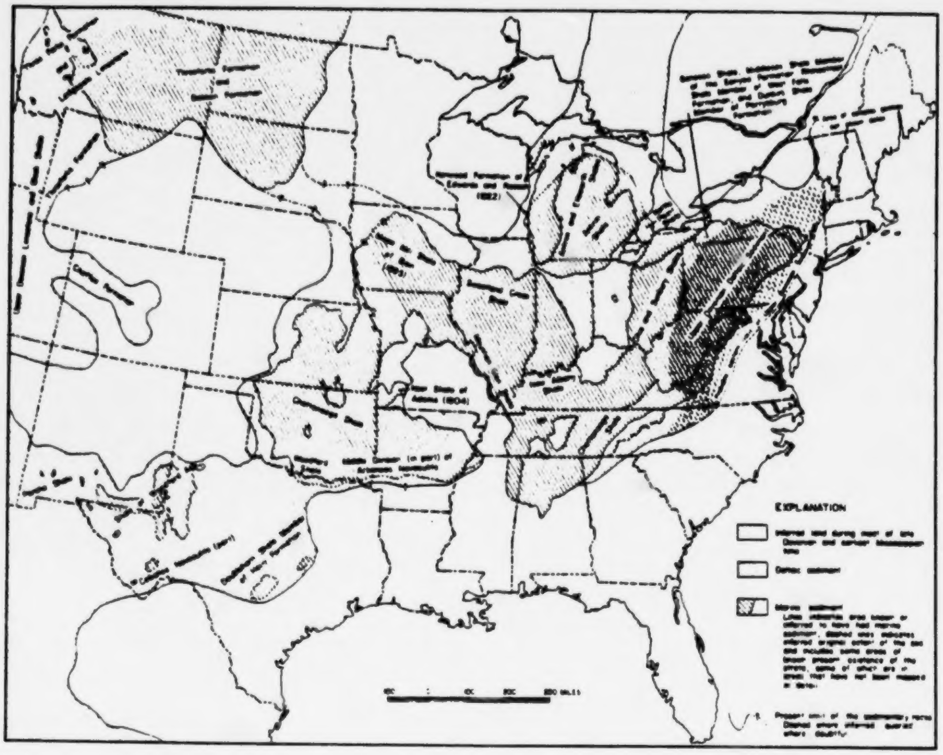


Figure 2.2-3. Distribution of Upper Devonian and Lower Mississippian Black Shales in the Eastern United States. Source: Baughman, 1978 (Reproduced with permission.)

organic content of more than 10 percent by weight, a unit rock thickness of at least 10 ft, an overburden thickness of less than 200 ft, and a stripping ratio of less than 2.5 to 1. The study assumed hydroretorting yields of 85 percent of the organic carbon present, and strip mining at 90 percent recovery of in-place shale.

2.2.3 Other Shale Deposits

Among other U.S. shale deposits are the thin strata of carbonaceous shales associated with coal beds, particularly in the Appalachian coal region. It is estimated that perhaps 60 billion bbl of equivalent oil may be present there in high grade shales assaying from 25 to 100 gal/ton. In California, the Miocene marine shales are believed to constitute a 70-billion bbl resource in shales varying from 5 to 25 gal/ton. In southwestern Montana, beds of Permian black shale, ranging from 5 to 15 gal/ton, may total up to 10 billion bbl of equivalent oil in place. As with the Appalachian coal shales, however, neither the Alaskan, California, nor the Montana shale are considered to be of near-term commercial importance [Duncan et al., 1965].

2.3 GEOLOGY

The geology of United States oil shales varies with the location of each occurrence. The geologic factors which are similar from deposit to deposit are related to the modes of origin for oil shales. The origin of oil shale involved the deposition of organic remains from quiescent organic-rich waters. The maintenance of reducing conditions during and after deposition and before induration was required to prevent oxidation of deposited organic matter. The similarities in geology appear to end at this point, as evidenced by the wide differences in the mineralogical composition of the inorganic fraction of oil shale and the variance of the properties of kerogen (altered organic material) from deposit to deposit.

Oil shale interest to date has concentrated on the Green River Formation deposits and more recently the Devonian-Mississippian black shale deposits. For this reason, discussions of the geology of these two major deposits are presented.

2.3.1 Green River Formation

The Green River Formation oil shales were deposited 50 to 60 million years ago in two large Eocene-age lakes. Lake Uinta occupied the northwest part of Colorado and the northeast part of Utah. Lake Gosiute occupied the southwest portion of Wyoming. During different periods of deposition of the Green River Formation the two lakes were probably connected in the area of northwest Colorado and southwest Wyoming near the east end of the Uinta Mountain Uplift.

Located within each of these ancient lake complexes were individual depositional basins. Fluctuations in lake levels caused by tectonic and climatic changes resulted in alternating deposition of oil shales, saline minerals, fluvial sediments, fresh water facies, and mud-flat type deposits. Figure 2.2-2, discussed previously, shows the individual depositonal basins. The thicker, richer oil shales are generally located at the depositional centers of these basins.

2.3.1.1 Piceance Creek Basin, Colorado

The Piceance Creek basin is a large asymmetric structural downwarp [Donnell, 1961]. The axis of the basin trends northwest to southwest with the western and southern flanks gently sloping into the basin. The northern and eastern flanks slope much more steeply into the basin. The basin is bordered on the northwest and north by the Rangely-Skull Creek-White River anticlinal trends; on the east by the White River Uplift; on the southeast and south by the Elk and West Elk Mountains and Gunnison Uplift; and along the west by the Douglas Creek arch [Murray et al., 1964]. Numerous small anticlines and synclines are found within the basin; faulting (graben) systems are associated with some of the more pronounced structural trends.

Strata exposed in and around the margins of the basin range in age from late Cretaceous to early Tertiary [Donnell, 1961]. The oldest rocks are the late Cretaceous Mesaverde Group which is composed of sandstones, shales, and some coal beds. Fossil content indicates that deposition occurred near standlines in fresh, brackish, and marine environments. The Mesaverde rocks are generally more resistant to erosion and form a series of prominent benches which outcrop continuously around the southern and eastern margin of the basin. Overlying the late Cretaceous is the Paleocene series consisting of the Ohio Creek Conglomerate and an unnamed unit, composed of feldspathic sandstones, shales, and thin coal beds, which is considered a Fort Union Formation equivalent. The Wasatch Formation of early Eocene overlies the Paleocene rocks and consists of thick sequences of lenticular sandstones and varicolored shales with some coal beds. Fossil evidence indicates that the Wasatch was deposited in a terrestrial fluvial environment. The Wasatch Formation, being less resistive to erosion than overlying and underlying strata, forms lowland areas between the cuestas of the more resistive adjacent rocks. The Green River Formation, containing the oil shales of the Piceance Creek basin, is generally thought of as overlying the Wasatch Formation. However, upper tongues of the Wasatch Formation are time equivalent to some Green River depositional sequences which represents either fluvial depositional encroachment into the lacustrine Green River environment or regression of the Green River lacustrine environment. Similarly, the fluvial (stream-bed) Uinta Formation intertongues, but generally overlies, the lacustrine (lake-bed) deposits of the Green River Formation. The Green River Formation in Piceance Creek basin has been divided into three main members based on lithology, but locally a fourth clastic facies is present. Each of the members is discussed in ascending order with emphasis on the Parachute Creek Member, the main oil shale bearing unit.

The Douglas Creek Member, basal member of the Green River Formation, is composed of sandstones, shales, and limestones that conformably overlie the varicolored shale and sandstone units of the Wasatch Formation. This member has been recognized only in the southern, western, and central parts of the basin. In the eastern part of the basin, aclastic facies replaces the Douglas Creek Member. To the northwest, the Douglas Creek Member coalesces with shales of the overlying Garden Gulch Member. Resistant strata of the Douglas Creek Member form a series of light brown benches along the base of the Green River Formation escarpment.

The Garden Gulch Member, overlying the Douglas Creek Member along the basin margins, is composed of dark, finely laminated illite shales and marlstone, some of which contain kerogen. With the exception of the eastern part of the basin, where equivalent sandy beds replace the member, it is present throughout the basin. The Garden Gulch outcrops as gray steep slopes between the white cliffs of the Parachute Creek Member and the brown and buff benches of the Douglas Creek Member.

Problems with the correlation of the Garden Gulch and Douglas Creek Members, as they were previously described at type sections on the flank of the basin, to central basin deposits as they are presently mapped has been discussed [Roehler, 1974]. The two members at the type sections have been described as being "...largely chronologic and lithologic equivalents." Others do not differentiate the two members because they are partly time-equivalent. The thickness of the Garden Gulch-Douglas Creek (undifferentiated fresh water unit) in the more central portion of the basin is reported to be at least 1,000 feet. Two easily discernible geologic markers in the subsurface, found on resistivity logs, exist in the vicinity of the Garden Gulch-Douglas Creek unit. Both markers exhibit an extremely low resistivity. The uppermost marker, the Blue marker, is considered the contact between the clay (illite) shales of the Garden Gulch and the dolomitic marlstones of the overlying Parachute Creek Member. The lowermost marker, the Orange marker, has been described by some as the contact between the Garden Gulch and Douglas Creek Members [Roehler, 1974].

A clastic facies equivalent to the Douglas Creek, Garden Gulch, and lower portion of Parachute Creek Members are assigned to the Anvil Points Member. This member is composed of sandstones, shales, marlstones, siltstones, and limestones. The Anvil Points Member has been described along outcrops from the Parachute Creek valley around the eastern rim, to a little north of the headwaters of Piceance Creek. The absence of the Anvil Points Member in the Piceance Creek gas field indicates that the member is confined to the southeast and eastern parts of the basin. The maximum known thickness is 1,870 feet in the upper Piceance Creek area. The Anvil Points Member appears as a series of benches and cliffs below the cliffs of the Parachute Creek Member. It interfingers with the overlying Parachute Creek Member and the underlying Wasatch Formation with both the upper and lower contacts conformable and gradational.

The Parachute Creek Member which overlies the Douglas Creek-Garden Gulch unit is of most interest because it contains the majority of the oil shale resources in the Piceance Creek basin. Although the term oil shale is used extensively, the lithology generally consists of kerogenetic dolomitic marlstone and differs considerably from the true illite shales of the underlying Garden Gulch Member. Weathering of the resistant Parachute Creek Member has produced precipitous and often spectacular escarpments around the rim of the basin. The thickness of the Parachute Creek Member varies from over 2,000 feet in the north central part of the basin to about 500 feet along the margins.

The most consistently rich and laterally persistent oil shale zone in the basin is designated the Mahogany ledge on outcrop and Mahogany zone in the subsurface [Bradley, 1931]. Figure 2.3-1, a schematic cross section, shows the relative position of the Mahogany zone as well as other members and zones within the Green River Formation. The very resistant-to-weathering nature of the Mahogany zone is due to its high kerogen content and results in vertical to near-vertical outcrops. The Mahogany zone is bounded on the top and bottom by relatively thin barren zones termed the 'A' and 'B' grooves, respectively. These barren zones are less resistant to erosion, forming slopes on outcrops that resemble grooves, hence their designation. In the subsurface both the 'A' and 'B' grooves produce distinct lows on resistivity logs. The thickness of the Mahogany zone ranges from approximately 100 feet near the margins of the basin to about 200 feet in the north central part of the basin. Generally, the grade of oil shale in the Mahogany zone exceeds 20 gallons per ton with the richest sequence comprising approximately 130 feet of 30 gallon per ton shale.

Above the Mahogany zone there generally is 300 to 500 feet of leaner oil shale. This sequence is thickest in the southern part of the basin. Due to interfingering with the overlying Unita Formation in the northern part of the basin, the upper sequence thins to less than 300 feet.

A sequence of oil shale below the Mahogany zone extends from the top of the Blue marker to the base of the 'B' groove. In the southeastern part of the basin this lower oil shale sequence is interfingered with, and in some instances replaced by, the Anvil Points Member. In the extreme northwest part of the basin the lower oil shale sequence is absent and the Mahogany zone and overlying oil shale rests conformably on the Garden Gulch Member (Donnell, 1961). Elsewhere, the thickness of the lower oil shale sequence ranges from a minimum of 20 feet in the southwest to over 1,300 feet in the north-central part of the basin. Toward the central portion of the basin the lower sequence of oil shale thickens due to the increased lacustrine type deposition, resulting in significant accumulations of dolomitic marlstones, organic material, and saline minerals. The saline minerals, depending on the particular mineral, have been found finely disseminated within the oil shale, as individual spherical crystal growths or rosettes and as bedded layers and zones.

The lower oil shale zone was subdivided into a series of alternating lean and rich zones [Cashion and Donnell, 1974] . The rich zones were designated R-4, R-5, R-6, etc. This designation and correlation was based on oil shale grade from the Modified Fischer Assay or apparent grade from geophysical logs. The lower oil shale sequence can also be subdivided into two zones, leached and unleached, on the basis of removal by dissolution or leaching of saline minerals, mainly consisting of minerals such as nahcolite

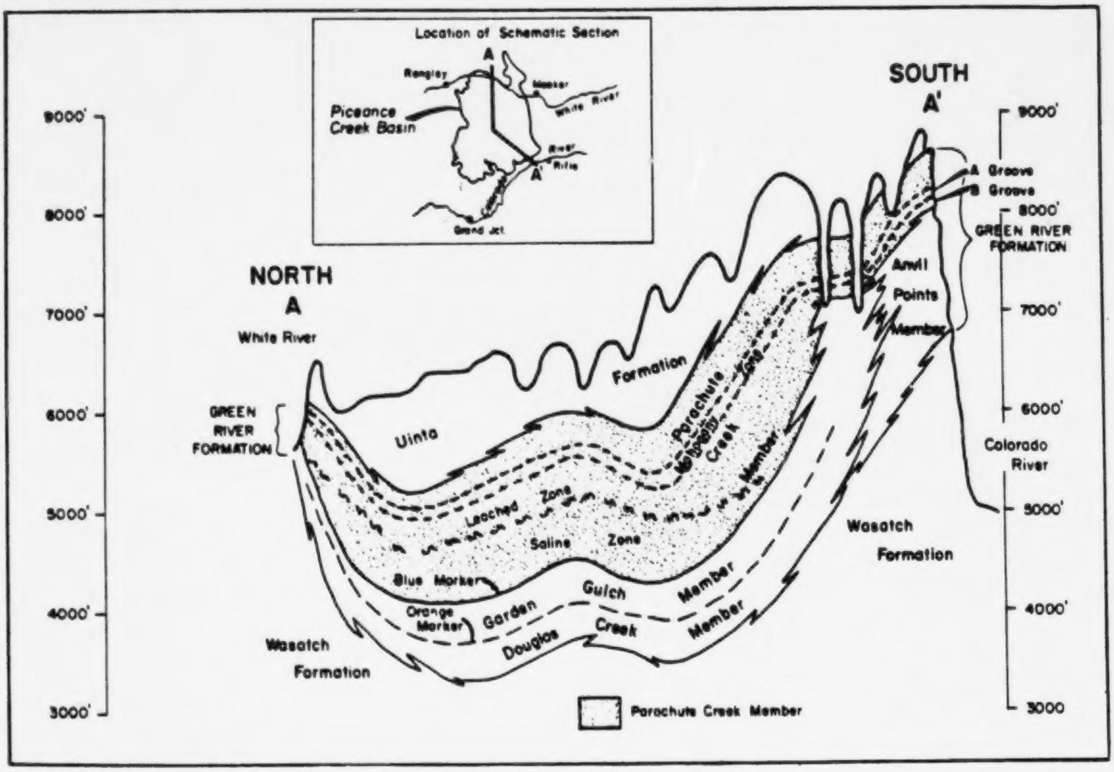

Location of Schematic Section
A
Rangley
Meeker
White River
Piceance Creek Basin
River
Rifle
A'
Grand Jct.
SOUTH
A'
9000'
8000'
7000'
6000'
5000'
4000'
3000'
A Groove
B Groove
GREEN RIVER FORMATION
Anvil Points Member
NORTH
A
White River
GREEN RIVER FORMATION
Uinta
Formation
Parachute Creek Member
Leached Zone
Saline Zone
Colorado River
Wasatch Formation
Blue Marker
Orange Marker
Garden Gulch Member
Douglas Creek Member
Wasatch Formation
Parachute Creek Member

Figure 2.3-1. Schematic North-South Cross Section of Piceance Creek Showing Relationship of Oil Shale Bearing Members of the Green River Formation and Surrounding Strata.
Source: Baughman, 1978 (Reproduced with permission.)

and halite in the upper portions of the saline section. Although leaching is not confined to any one area of the basin, the effects of leaching are most pronounced in the central part of the basin where there was maximum saline deposition. An unleached or saline zone is found below the leached zone in the central portion of the basin. This zone contains potentially recoverable deposits of nahcolite and dawsonite. From these two minerals, soda ash and alumina can be produced. The thickness of the unleached saline zone in the central part of the basin ranges from about 500 to over 1,000 feet.

The interface of the leached and unleached zone, somewhat poorly defined, is termed the dissolution surface. In reality, it is probably a dissolution zone, as numerous cores have shown nahcolite to be present above the dissolution surface while vugs and cavities are found below. At best, any designated dissolution surface is an approximation.

The leached zone is characterized by cavities, vugs, and collapsed breccia. The thickness of the leached zone toward the central part of the basin varies from about 400 to 1,100 feet. Leached zone thickness is greater around the margins of the major saline deposition. Leaching of the saline minerals has upgraded the oil shale value within the leached zone by removing inorganic saline minerals which would have had the effect of diluting the percentage of organic material. Leaching has also produced higher porosity and permeability by removing evaporites thus producing an aquifer while reducing bulk strength of the rock.

Overlying the Green River Formation is the Uinta Formation, which includes sandstones and siltstones which were formerly designated as the Evacuation Creek Member of the Green River Formation. With the exception of a few local unconformities described by Donnell (1961), these formations represent a continuous depositional sequence. The outcrop of the Uinta Formation forms a buff to rusty brown colored rounded cap receding from the white cliffs of the Parachute Creek Member.

The maximum thickness of the Uinta Formation is unknown because the top has been removed by erosion; however, from subsurface information, it is known to exceed 1,200 feet. Because of intertonguing with the Parachute Creek Member, the lower boundary varies from location to location.

2.3.1.2 Uinta Basin, Utah

The Uinta basin is sharply asymmetrical, the axis of which lies in the northern portion of the basin trending east-west and parallel to the Uinta Mountain uplift which borders the basin to the north. The Wasatch Mountains border the basin to the west and the Douglas Creek Arch borders the basin on the East. The southern flank of the basin is bordered by the San Rafael Swell, the Salt Creek Anticline, and the Uncomphagre Uplift. Over 13,000 feet of sediments were deposited in the basin center during the Eocene time. Eocene strata of the Uinta basin belong to the Wasatch Green River, and Uinta Formations, consisting of rocks deposited in fluvial and lacustrine type environments. The thickest and richest oil shales of the Uinta basin are found in the east central portion of the basin, as indicated on Figure 2.3-2.

The Wasatch Formation, the basal Eocene strata, is composed of fluvial sandstones, shales, mudstones, and siltstones. The Wasatch rocks vary in color from red and purple to browns and light grays. The formation is divided into two parts, the main body of the Wasatch and the Renegade tongue which intertongue with the overlying Green River Formation.

The Green River Formation is divided into three members in the Uinta basin: the basal Douglas Creek Member; and the overlying Garden Gulch Member, and the uppermost Parachute Creek Member. Figure 2.3-2 is a schematic cross section illustrating the Eocene stratigraphy of the Uinta basin.

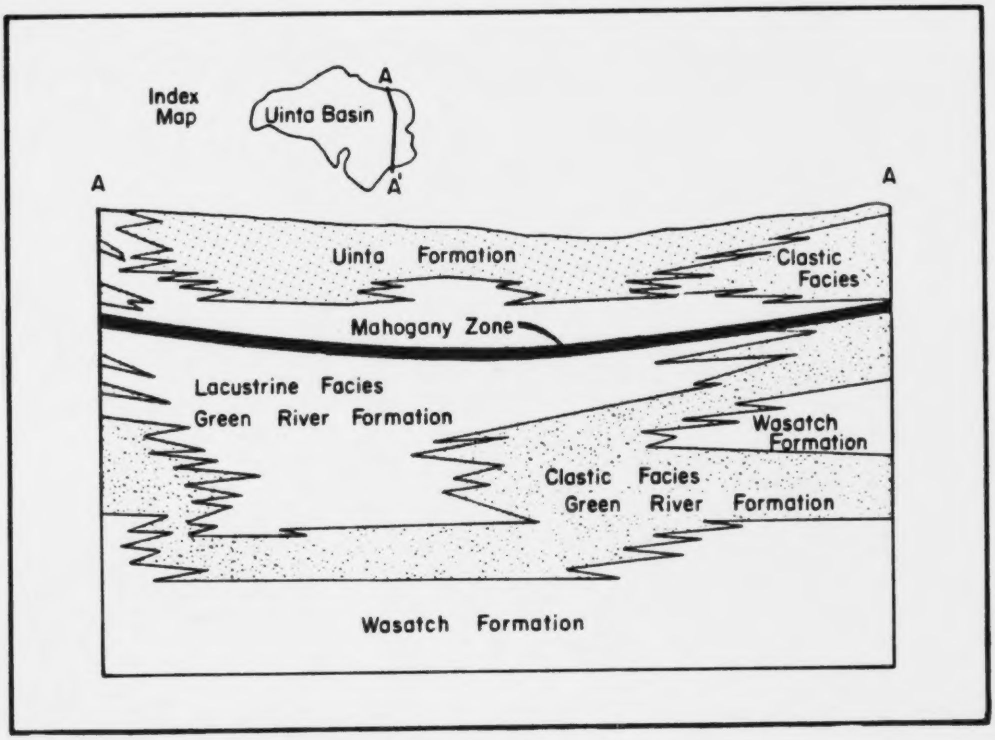

Index Map
Uinta Basin
A
A'
A
A
Uinta Formation
Clastic Facies
Mahogany Zone
Lacustrine Facies Green River Formation
Wasatch Formation
Clastic Facies Green River Formation
Wasatch Formation

Figure 2.3-2. Schematic Cross Section of Uinta Basin Showing Relationship of Oil Shale Bearing Green River Formation With Surrounding Strata.
Source: Baughman, 1978 (Reproduced with Permission.)

The Douglas Creek Member is composed of shale, siltstone, sandstone, and oolitic, algal, and ostracodal limestones. Locally, the Douglas Creek Member contains a few oil shale beds. The member conformably intertongues with fluvial sediments of the Wasatch Renegade Member. The maximum thickness of the member is 1,180 feet [Cashion, 1967].

The Garden Gulch Member outcrop is distinctly different from the Douglas Creek Member outcrop, as the Garden Gulch forms gray slopes which contrast with the brown ledge-forming sediments of the Douglas Creek Member. The member is chiefly composed of marlstones, oil shales, and siltstones. The Garden Gulch Member is thickest along the eastern outcrop of the Green River Formation of the Uinta basin. Westerly, the Garden Gulch thickens, while the overlying Parachute Creek and underlying Douglas Creek members thicken basinward. The maximum thickness of the Garden Gulch Member is 230 feet [Cashion, 1967].

The Parachute Creek Member of the Green River Formation contains the oil shales of significant interest in the Uinta basin. The member is composed mostly of kerogenetic marlstone (oil shale), barren marlstone, sandstone, siltstone, and tuff. The oil shales are for the most part finely laminated or varved. Individual beds within the Parachute Creek Member are well known for their lateral extent and relative continuity. Many of the mappable units of the Piceance Creek basin oil shales are also recognized and mappable in the Uinta basin. The thickest and richest sequence of oil shale in the Uinta basin is found in the laterally persistent Mahogany ledge, termed Mahogany zone in the subsurface. Oil shale also exists above and below the Mahogany zone, but is somewhat leaner in grade. The maximum thickness of the Mahogany zone in Utah is about 100 feet. The Parachute Creek Member is about 750 feet thick in the east central portion of the basin but thickens to the north and west toward the synclinal axis of the basin. Evidence of a saline zone exists in the upper one-third of the member, where crystal cavities thought to have once contained the mineral nahcolite have been observed. The leaching of the nahcolite by groundwater has given the appearance on vertical outcrops that swallows have nested there, thus giving rise to the name "birds nest zone" [Cashion, 1967]. The upper section of the Parachute Creek Member containing the "birds nest zone" was named Evacuation Creek Member [Bradley, 1931 and Cashion, 1967]. However, the nomenclature has since been revised to place those sediments within the Parachute Creek Member [Cashion et al., 1974]. The lacustrine sediments of the Parachute Creek member intertongue with the overlying fluvial sediments of the Uinta Formation.

Overlying the Green River Formation is the Uinta Formation, which consists of approximately 1,750 feet of sandstones and claystones. Colors range from brown and greenish gray in the lower section to browns and reds, in the upper section [Cashion, 1967]. The Uinta Formation covers most of the east central portion of the Uinta basin where the thicker and richer oil shales are found.

2.3.1.3 Green River and Washakie Basins, Wyoming

Ancient Lake Gosiute covered a large portion of southwestern Wyoming. The large lake was bordered to the north by the Sweetwater Uplift, the Wind River Uplift, and the Gros Ventre Uplift. To the west, the lake was bordered by highlands created by the Absaroka Thrust, the Uinta Arch, and the White River Uplift. The

Park Range and Rawlins Uplift border the lake to the east. The oil shales of primary interest in Wyoming are located in the Green River and Washakie basins, which are contained within the areal extent of ancient Lake Gosiute. Other smaller basins within the extent of Lake Gosiute also contain oil shale but they are thin and lean in comparison to those of the Washakie and Green River basins. The other basins are the Fossil basin, Great Divide basin, and the Sand Wash basin, the latter extending into Northwestern Colorado. The Washakie and Green River basins are now separated by the Rock Springs Uplift, similar to the separation of the Uinta basin and Piceance Creek basins by the Douglas Creek Arch.

The stratigraphy of the sediments containing the oil shales in Wyoming is similar to that containing oil shales in Colorado and Utah. The Wasatch Formation underlies the oil shale bearing Green River Formation. The Wasatch in Wyoming, as in Colorado and Utah, consists predominently of fluvial varicolored brown and gray sandstones, siltstones, shales, and mudstones. Upper Wasatch sediments intertongue with the overlying Green River Formation. The Green River Formation has been divided into four basic members, in ascending order: Luman Tongue, Tipton Shale, Wilkins Peak, and the Laney Shale Member. The fluvial Bridger Formation overlies and intertongues with the Green River Formation. Figure 2.3-3 is a schematic section, showing the general east-west stratigraphic relationship of the rocks deposited during Eocene time in the Green River and Washakie basins.

Each of the members of the Green River Formation represents widespread deposition of lacustrine facies of ancient Lake Gosiute. The Luman Tongue contains only lean oil shales. The Tipton Member contains oil shales considerably richer than those of the Luman in the Green River basin.

The Wilkins Peak Member consists mostly of marlstones, siltstones, saline deposits, and oil shale. The saline section of the Wilkins Peak Member contains bedded deposits of the mineral trona, from which soda ash is produced. The trona is presently being mined and processed. This saline section of the Wilkins Peak member correlates time-wise with the saline section of the lower Parachute Creek Member in the Piceance Creek basin [Roehler, 1974]. The oil shales of the Wilkins Peak Member, although relatively rich, are thin and separated by lean or barren marlstones. The Wilkins Peak Member grades laterally to gray-green marlstones and is eventually replaced in section by fluvial tongues of the Wasatch Formation.

The uppermost member of the Green River Formation in Wyoming is the Laney Member. The widespread distribution of the Laney indicates that Lake Gosiute was most extensive during Laney deposition. Oil shales of the Laney Member in the eastern part of the Washakie basin represent the thickest and richest oil shale

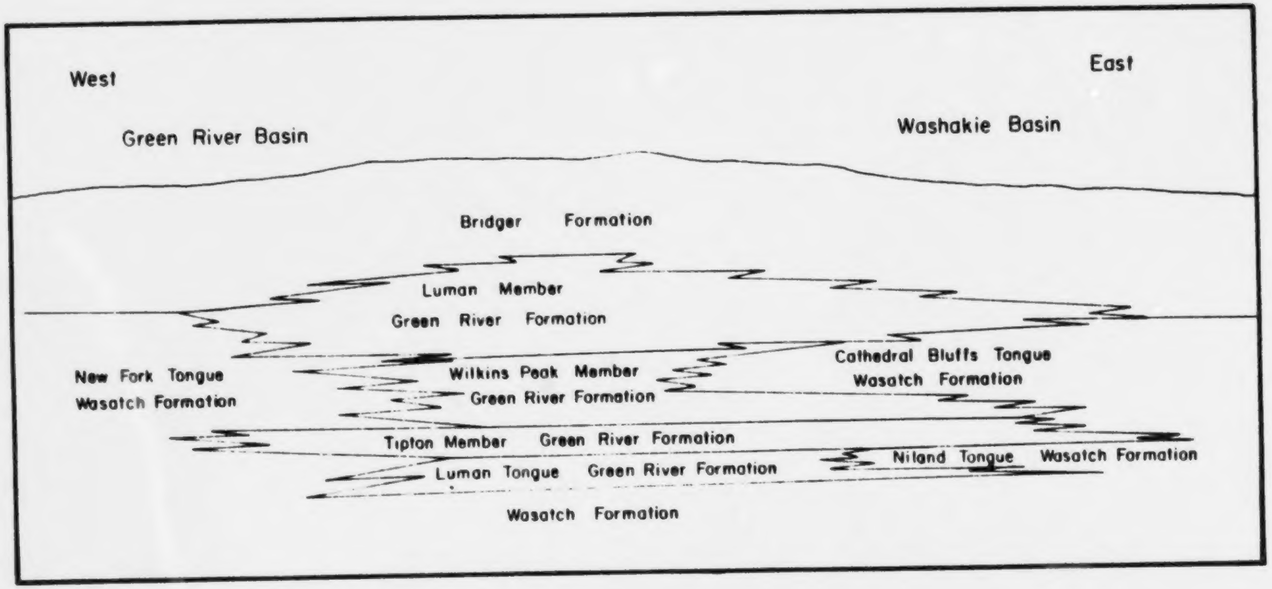

West
East
Green River Basin
Washakie Basin
Bridger Formation
Luman Member
Green River Formation
Cathedral Bluffs Tongue
Wasatch Formation
New Fork Tongue
Wasatch Formation
Wilkins Peak Member
Green River Formation
Tipton Member Green River Formation
Niland Tongue Wasatch Formation
Luman Tongue Green River Formation
Wasatch Formation

Figure 2.3-3. Schematic Cross Section Showing Relationship of Green River Formation with Surrounding Strata.
Source: Baughman, 1978 (Reproduced with permission.)

deposit in Wyoming. The section of oil shale varies from about 150 to 500 feet in thickness [Roehler, 1973]. The oil shales of the Laney Member in the Green River basin are not as thick as those of the Washakie basin. The lacustrine Laney Member intertongues with the overlying fluvial Bridger Formation.

Figures 2.3-4, 2.3-5, and 2.3-6 show the areal distribution of the richer oil shale beds of the Green River basin [Culbertson, 1968]. Accompanying histograms indicate the grade of oil shale within the Tipton, Wilkins Peak, and Laney Members of the Green River Formation.

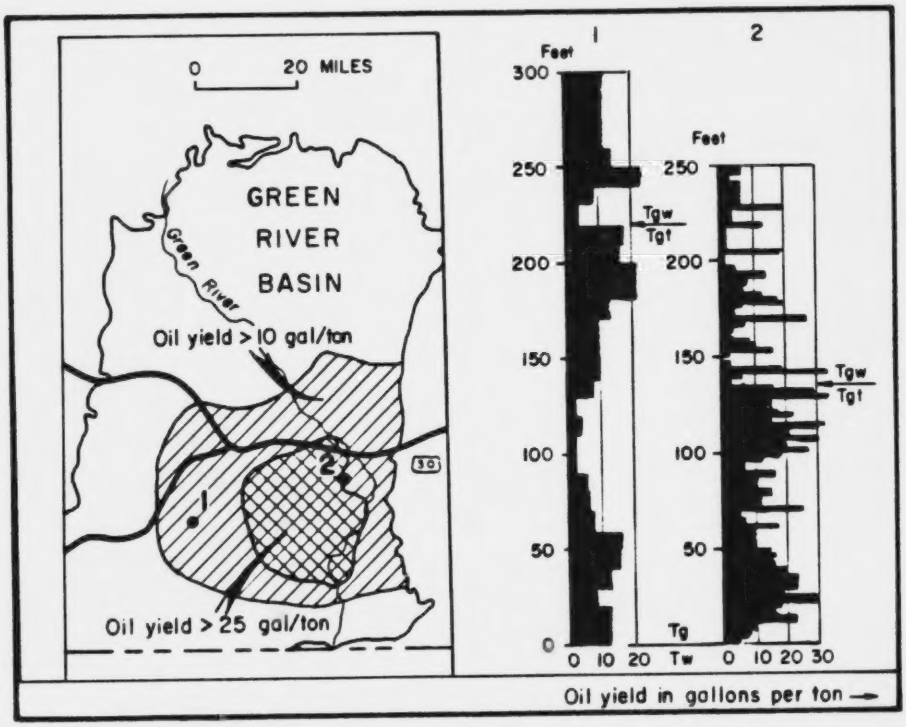
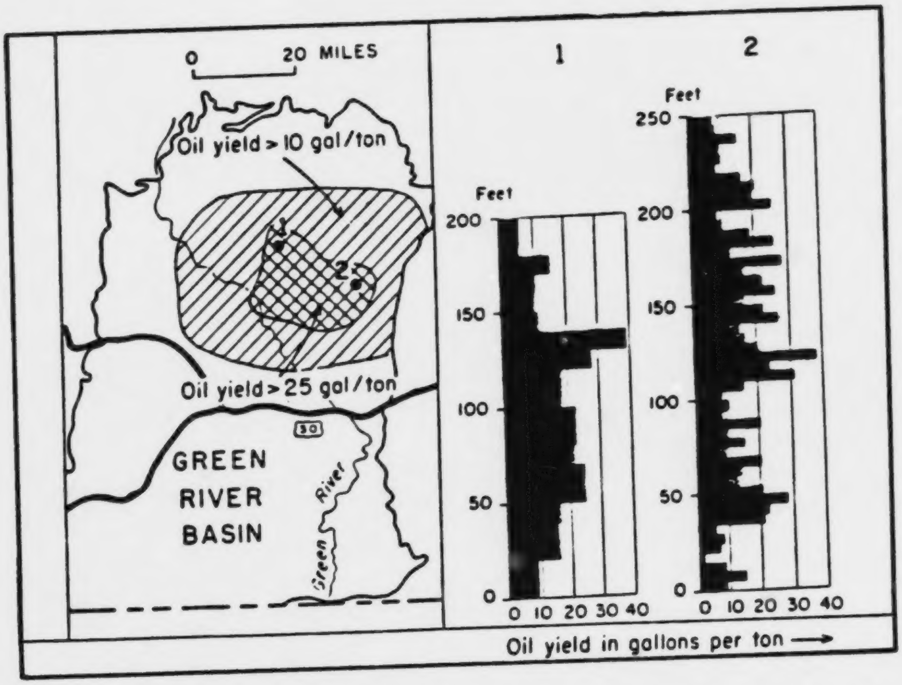

0 20 MILES
GREEN RIVER BASIN
Green River
Oil yield > 10 gal/ton
Oil yield > 25 gal/ton
30
1
2
Feet
300
250
200
150
100
50
0
Tgw
Tgt
Tg
Tw
0 10 20
0 10 20 30
Oil yield in gallons per ton →

Figure 2.3-4. Oil Yield of Tipton Shale Member.
Source: Baughman, 1978 (Reproduced with permission.)

2.3.2 Devonian And Mississippian

Until quite recntly there has been only limited research on the black shales of the East and Midwest because of the emphasis on the richer and thicker oil shales of the Green River Formation. The term "black shale" refers to dark (principally black or dark gray) shale deposits which owe their dark color to their organic content and which were generally deposited under marine conditions.



0 20 MILES
Oil yield > 10 gal/ton
Oil yield > 25 gal/ton
30
GREEN RIVER BASIN
Green River
1
2
Feet
250
200
150
100
50
0
0 10 20 30 40
Oil yield in gallons per ton →

Figure 2.3-5. Oil Yield of Wilkins Peak Member. Source: Baughman, 1978 (Reproduced with permission.)

Figure 2.2-1, referred to previously, indicates the areas under which the black shale of Devonian and Mississippian are known and inferred to exist. Total land area indicated is nearly 400,000 square miles. The crosshatched areas contain the black shales area bounded by the dashed line indicates where the location of the black shales are uncertain or where it is concealed (i.e., buried) [Duncan et al., 1965].

As may be noted, these black shales are widely distributed between the Rocky Mountains and the Appalachian Mountains, with the principal known resources contained in zones five or more feet thick and correlatable in Arkansas, Illinois, Indiana, Kentucky, Michigan, Ohio, Oklahoma, Tennessee, and Texas [Conant et al., 1961].

Depending upon the location, various formation names have been applied to the black shales of the upper Devonian and lower Mississippian. They include the Chattanooga, Antrim, New Albany, Dunkirk, Mountain Glen, Woodford, and the Lodgepole [Conant et al., 1961].

Figure 2.2-3 illustrates the depositional conditions existing during the Devonian and Mississippian. The figure also shows the different names applied to the "black shales" deposited during this time [Conant et al., 1961].

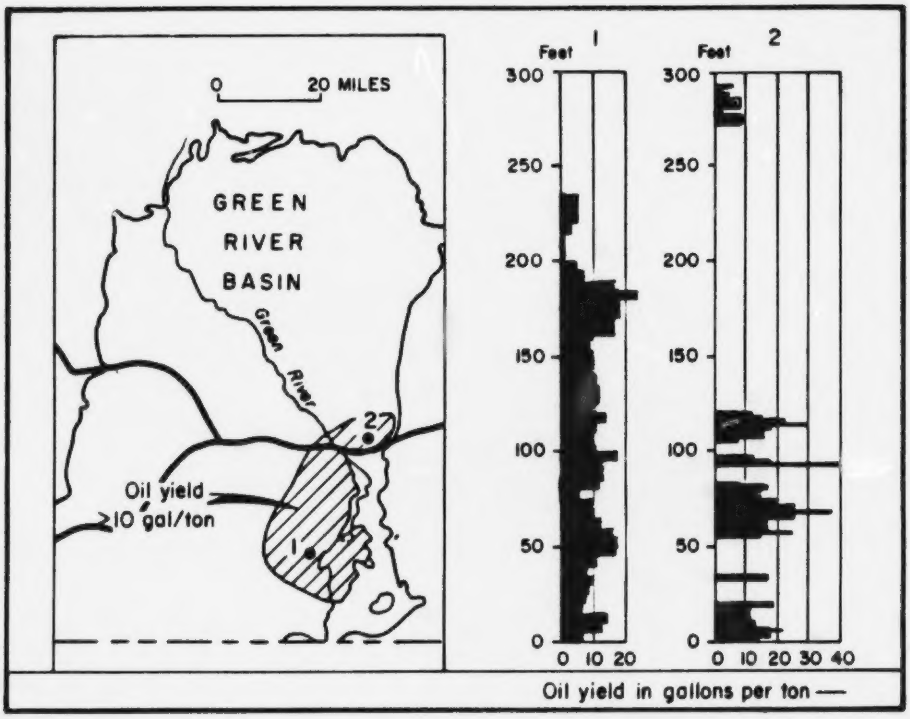


Figure 2.3-6. Oil Yield of Laney Shale Member. Source: Baughman, 1978 (Reproduced with permission.)

Basically, the area of deposition was in the Paleozoic Appalachian Sea, which covered the Appalachian, Ohio, and Michigan basins. Circulation of marine water carrying abundant mineral organic matter was enhanced by outlets from the Appalachian Sea via the St. Lawrence seaway and by a southern opening into the Mexico Mediterranean. Under sediment loading, the basins continued to subside, and correspondingly more sediments were deposited, compressing and forcing the black shales deeper into their respective basins. Such conditions existed until the end of the Paleozoic when the entire eastern part of the continent was emergent [Conant et al., 1961].

The black shales of the Devonian and Mississippian, in contrast to the oil shales of the Green River Formation, are true shales composed dominantly of the micaceous clay illite.

Other important minerals associated with the black shales include phosphate and uranium minerals, with uranium ranging in concentration from 0.001 to 0.008 weight percent. These minerals are found in the Chattanooga formation.

2.4 COMPOSITION

2.4.1 Minerals

The proportions of inorganic and organic minerals in oil shale vary with the grade of shale. Typical values are shown in Table 2.4-1 [Stanfield, 1951]. Typical of the minerals present in Green River oil shale of commercial grade is the listing presented in Table 2.4-2 [Smith et al., 1978].

TABLE 2.4-1. MINERAL CONTENT OF GREEN RIVER OIL SHALE VERSUS GRADE

Fischer Assay, gallon oil/ton	10.5	26.7	36.3	57.1
Inorganic minerals, wt., %	92.2	84.0	80.1	67.0
Organic minerals, wt., %	7.8	16.0	19.9	33.0
Oil Shale	100.0	100.0	100.0	100.0

Source: Stanfield, 1951

TABLE 2.4-2. AVERAGE MINERAL COMPOSITION OF MAHOGANY ZONE SHALE, COLORADO AND UTAH

Mineral	Chemical formula	Composition weight percent
Dolomite	$(Mg,Fe)Ca(CO_3)_2$	32
Calcite	$CaCO_3$	16
Quartz	SiO_2	15
Illite	$KAl_2(AlSi_3)O_{10}(OH)_2$	19
Albite	$NaAlSi_3O_8$	10
K feldspar	$KAlSi_3O_8$	6
Pyrite	FeS_2	1
Analcime	$NaAlSiO_4 \cdot 25H_2O$	1
	TOTAL	100

Source: Smith et al., 1978

The chemical analyses of the inorganic mineral portions of 16 samples of Green River oil shale varying in grade from 10.5 to 75.0 gallons per ton were reported [Stanfield, 1951]. The minimum, maximum, and average values are shown in Table 2.4-3. The variation of inorganic chemical composition with shale grade is shown in Table 2.4-4, along with the inorganic chemical composition of the spent shale.

TABLE 2.4-3. FISCHER ASSAY DATA OF THE INORGANIC MINERAL PORTIONS OF 16 SAMPLES OF GREEN RIVER OIL SHALE RANGING FROM 10.5 to 75.0 gal/ton OIL SHALE

Assay data, %	Minimum	Maximum	Average
SiO_2	21.1	40.9	27.6
Fe_2O_3	2.3	4.3	2.9
Al_2O_3	5.3	9.5	7.7
CaO	8.2	21.2	13.9
MgO	3.8	8.7	5.9
SO_3	0.1	2.6	1.4
Na_2O	1.0	2.7	2.1
K_2O	0.9	3.4	1.5
Sub Total	--	--	63.0
Mineral CO_2 in raw shale	9.9	25.7	17.4
Mineral CO_2 in spent shale calculated to raw shale	9.7	25.6	17.0
Mineral CO_2 in raw shale that was volatilized by the assay	0.0	10.2	2.3

Source: Stanfield, 1961

Particle size measurements showed that 99.4 percent of the inorganic constituents of the Green River oil shales are smaller than 44 microns (325 mesh sieve), about 80 percent are smaller than 10 microns, and about 10 percent are smaller than 0.5 micron [Tisot, 1963]. Table 2.3-5 presents the typical mineralogical composition of Devonian black shale [Bates et al., 1957].

2.4.2 Kerogen

Kerogen is that portion of the organic material in oil shale that is insoluble in ordinary solvents for petroleum and that, upon the application of heat, yields gas, oil, bitumen, and organic residue (mainly fixed carbon). Bitumen, a benzene-soluble material generally comprises a small part of the total organic matter in oil shale. The term kerogen is often used, however, to denote the total organic material in oil shale.

Kerogen appears black in color to the unaided eye. Under the microscope, thick sections of kerogen appear yellow in color, with a minor portion appearing brown or black. It has no well defined structure, appearing as stringers, masses, and irregular granules all intermixed with the inorganic minerals in the rock.

TABLE 2.4-4. CHEMICAL COMPOSITION OF THE INORGANIC PORTION OF VARIOUS GRADES OF GREEN RIVER OIL SHALE AND OF THE SPENT SHALE PRODUCTS

Chemical constituent	Very low-grade shale (10.5 gal/ton)	Medium grade shale (26.7 gal/ton)	High-grade shale (36.3 gal/ton)	Very high-grade shale (61.8 gal/ton)
Raw shale				
SiO_2, percent	40.9	26.1	25.5	26.4
Fe_2O_3	4.3	2.6	2.9	3.1
Al_2O_3	9.4	6.5	6.3	7.0
CaO	11.0	17.5	14.2	8.3
MgO	5.4	5.3	5.6	4.5
SO_3	0.1	0.6	1.2	1.4
Na_2O	1.8	2.6	2.7	1.9
K_2O	3.4	1.0	1.9	1.0
Spent shale				
SiO_2	53.27	41.90	42.36	49.19
Fe_2O_3	5.64	4.10	4.74	5.87
Al_2O_3	12.28	10.53	10.46	13.13
CaO	14.82	28.11	23.54	15.40
MgO	7.00	8.53	9.30	8.35

Source: Stanfield, 1961

TABLE 2.4-5. TYPICAL MINERALOGICAL COMPOSITION OF DEVONIAN BLACK SHALE

Mineral	Composition weight percent
Quartz	22
Feldspar	9
Illite + minor kaolinite and muscovite	31
Carbon	13.6
Total organic matter	16 - 22
Pyrite and marcasite	11
Chlorite	2
Iron oxides	2
Tourmaline, zircon, and apatite	1

Source: Bates et al., 1957

The organic matter content of oil shale increases with the grade of shale. Reported values are plotted on Figure 2.4-1 to show the range in organic content of shales varying from 10 to 75 gallons per ton in grade, as determined by the Modified Fischer Assay.

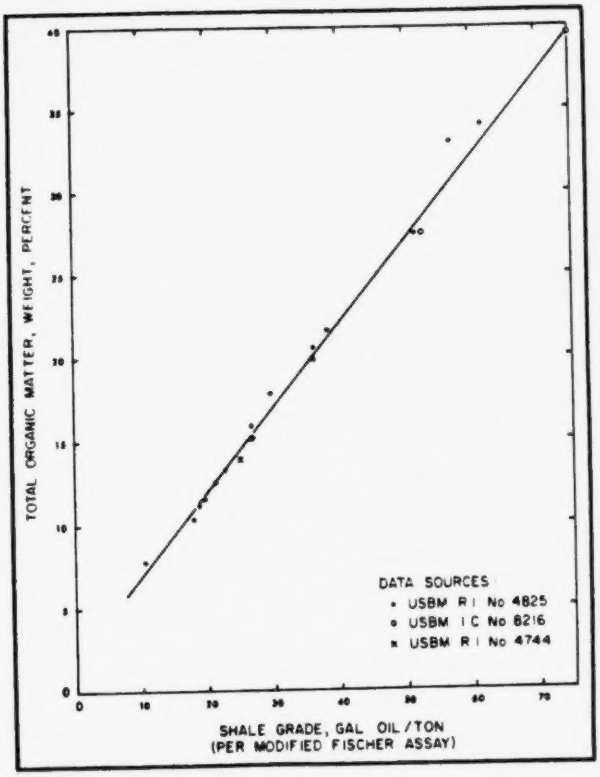


Figure 2.4-1. Organic matter content of Green River Oil Shales.
Source: Baughman, 1978 (Reproduced with permission.)

2.4.2.1 Composition of Kerogen

Ultimate

The ultimate composition of the organic material in ten samples of cores of Mahogany zone oil shale from Colorado and Utah have been reported [Smith, 1961]. The similarity among the compositions was striking. An average of the ultimate compositions of the samples was taken to represent the typical composition of the organic matter of Mahogany zone oil shales of the Green River Formation. This average composition is shown in Table 2.4-6.

TABLE 2.4-6. PROBABLE COMPOSITION OF MAHOGANY-ZONE ORGANIC MATTER

Component	Average amount of component, wt. % of organic matter
Carbon	80.52
Hydrogen	10.30
Nitrogen	2.39
Sulfur	1.04
Oxygen	5.75
C/H ratio	1.42

Source: Smith, 1961

A similar analysis was performed on New Albany shale [Smith and Young 1967]. The composition determined from this investigation is shown in Table 2.4-7.

TABLE 2.4-7. ELEMENTAL COMPOSITION OF NEW ALBANY SHALE ORGANIC MATTER

Component	Average (weight % organic matter)
Carbon	82.0
Hydrogen	7.4
Nitrogen	2.3
Sulfur	2.0
Oxygen	6.3

Source: Smith and Young, 1967

Carbon-hydrogen Ratio Comparisons

The approximate ratio of carbon to hydrogen (C/H) in the organic matter from both Green River and New Albany oil shale is compared to the C/H ratio of various other organic materials in Table 2.4-8.

TABLE 2.4-8. APPROXIMATE CARBON/HYDROGEN RATIOS IN VARIOUS ORGANIC MATERIALS

Material	C/H ratio
Conventional petroleum	6.2 - 7.5
Athabasca bitumen	7.5
Green River Kerogen	7.8
New Albany Organic Matter	11.1
Gilsonite	8.3
Lignitic coal	12.1
Low volatile bituminous coal	19.4
Anthracitic coal	35.1

Source: Baughman, 1978

Particle Bonding

Tests on surface area led to the conclusion that perhaps only a small amount of the organic matter is either directly or chemically bonded to the inorganic mineral constituents. Green River Formation kerogen can be found either partly or entirely encasing the inorganic mineral constituents of oil shale [Tisot, 1963]. Despite this conclusion, bonding between kerogen and inorganic matter is such that kerogen has never been isolated in pure form by either mechanical or chemical separatory processes.

Chemical Formula

Based on the elemental analysis of kerogen from Green River oil shale the following empirical formula was developed for the material: $C_6H_{9.8}N_{0.18}S_{0.04}O_{0.56}$ [Stanfield, 1951]. This formula is in substantial agreement with that reported later: $C_{215}H_{330}O_{12}N_5S$ [Vanderborgh, 1974]. The latter formula indicates a molecular weight of approximately 3200. It should be noted that these formulas are based only on the elemental analysis of samples, and they are not necessarily applicable for use in generallized correlations relating molecular weight to thermal or physical properties.

2.4.2.2 Specific Gravity

The probable specific gravity of kerogen in Green River oil shale has been reported as 1.07 [Smith, 1969].

2.4.3 Saline Minerals

The Tertiary-age sedimentary Green River Formation oil shale is a very complex material. In addition to its organic matter content, it contains literally hundreds of inorganic minerals. Among the inorganic minerals is an interesting collection of saline minerals. Saline minerals are defined as those minerals having sodium occupying one or all of their cation positions and the carbonate radical supplying all or part of the negative charge [Fahey, 1962]. The saline minerals in Green River oil shale, sometimes referred to as "associated" minerals, were formed in place during lithification of the sediments. They are of importance because of their potential value as co-products which may be produced while processing oil shale for recovery of liquid and gaseous fuels.

A compilation of the authigenic (formed in place) sodium minerals in the Green River Formation is presented in Table 2.4-9. The list includes sodium water-soluble minerals in addition to "saline" minerals. Some of these authigenic minerals are unique to the Green River Formation, while others are known only in rocks of igneous or metamorphic origin.

Trona is found only in Green River oil shales in Wyoming, occurring in a 500 square mile area west and northwest of Green River, Wyoming. Trona is mined from bedded deposits by four companies, which produce from it over 50 percent of the United States' supply of soda ash (NA_2CO_3). During 1977, over eight million tons of soda ash were produced from trona.

Bedded deposits of relatively pure trona mineral and occurrences of the sodium salts shortite, northupite, pirssonite, gaylussite, and bradleyite were first shown in the cores from the John Hay, Jr., well No. 1 in 1939. The first trona bed noted was about ten feet thick. Subsequent drilling showed it extended over an area of at least 60 square miles. About 67 billion tons of trona are contained in 24 beds more than three feet thick in the Wilkins Peak Member of the Green River Formation in southwest Wyoming [Culbertson, 1966]. These beds lie at depths of 400 to 3500 feet in a 1400 square mile area.

Another 36 billion tons of mixed trona and halite are reported by Culbertson to occur in 14 beds of more than three feet thickness in the southern part of the area. Occurrences of the mineral trona have been noted only in the Wyoming portion of the Green River Formation.

TABLE 2.4-9. AUTHIGENIC SODIUM MINERALS IN THE GREEN RIVER FORMATION

Mineral name	Chemical formula
Carbonates	
Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
Eitelite[a]	$Na_2Mg(CO_3)_2$
Dawsonite[b]	$Na_3Al(CO_3)_3 \cdot 2Al(OH)_3$
Burbankite[b]	$Na_2(Ca, Si, Ba, Ca)_4(CO_3)_5$
Shortite[a]	$Na_2Ca_2(CO_3)_3$
Pirssonite[b]	$Na_2Ca(CO_3)_2 \cdot 2H_2O$
Gaylussite	$Na_2Ca(CO_3)_2 \cdot 5H_2O$
Norsethite[a]	$BaMg(CO_3)_2$ (Check formula, no sodium shown)
(New Unnamed)	$3NaHCO_3 \cdot Na_2CO_3$
Nahcolite	$NaHCO_3$
Thermonatrite	$Na_2CO_3 \cdot H_2O$
Carbonate-phosphates	
Bradleyite[a]	$Na_3PO_4 \cdot MgCO_3$
Carbonate-chlorides	
Northupite	$Na_2CO_3 \cdot MgCO_3 \cdot NaCl$
Silicates	
Albite	$NaAlSi_3O_8$
Analcite	$NaAlSi_2O_6 \cdot H_2O$
Sepiolite	$H_6Mg_8Si_{12}O_{30}(OH)_{10} \cdot 8H_2O$ (Check formula, no sodium shown)
Loughlinite[a]	$Na_2Mg_3Si_6O_{16} \cdot 8H_2O$
Labuntsovite[b]	$(K, Ba, Na, Ca, Mn) (Ti, Nb) (Si, Al)_2(O, OH)_7H_2O$
Acmite[b]	$Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$
Elpidite[b]	$Na_2ZrSi_6O_{15} \cdot 3H_2O$
Magnesioriebeckite (crocidolite), etc.	$Na_2(Mg, Fe)_3(Fe, Al)_2Si_8O_{22}(OH)_2$
Feldspar	Variable composition
Borosilicates	
Reedmergnerite[a]	$NaBSi_3O_8$
Searlesite	$NaBSi_2O_6 \cdot H_2O$
Leucosphenite	$CaBaNa_3BTi_3Si_9O_{29}$
Halides	
Neighborite[a]	$NaMgF_3$
Cryolite	Na_3AlF_6
Halite	$NaCl$

[a] Unique to Green River Formation

[b] Known elsewhere only in igneous or metamorphic rocks.

Source: Jaffe, 1962

Organic acids of high molecular weight have been found in dark-colored trona mineral brines from wells drilled in the Eden-Farson area, approximately 40 miles north of Rock Springs, Wyoming. Both the dissolved trona and the dissolved organic matter are contained in the Green River Formation.

Nahcolite occurrences are common in Colorado and Utah oil shales, but are not noted in Wyoming shales. In Colorado's Piceance Creek basin, bedded deposits of the water soluble sodium salt nahcolite ($NaHCO_3$) were discovered from examination of core samples drilled in 1964 on Marathon Oil Company property in the north-central portion of the basin. Subsequent drilling disclosed three principal bedded units of nahcolite which occur at depth in a thickness from one to nine feet. Nahcolite in disseminated form has even greater distribution. Reserves of approximately 130 million tons of nahcolite per square mile have been estimated. [Hite et al., 1967].

The potential exists for recovery of nahcolite from oil shale formations by *in situ* leaching, by leaching from mined and crushed oil shale, or by mining directly from bedded deposits.

Nahcolite may find commercial markets as a chemical reactant which removes sulfur dioxide from stack gas streams, particularly those streams associated with coal-fueled electric power generating plants. An obvious market for nahcolite is as the raw material from which commercial-grade soda ash may be produced. A minor market may be for household use as high-purity sodium bicarbonate.

The mineral dawsonite, a sodium-aluminum carbonate, was noted to occur in great quantities in Colorado oil shale [Smith, 1963]. Dawsonite occurrences show great vertical and areal distribution in the northern (deeper) portions of the Piceance Creek basin, the zone ranging from 900 feet to 1900 feet below the surface. In place reserves of 42 million tons of alumina (recoverable from the mineral dawsonite) per square mile in the area of the Juhan corehole have been reported [Hite, 1967].

With proper heat treatment, avoiding temperatures high enough to promote chemical reaction between silicon dioxide and alumina (Al_2O_3), dawsonite can be converted to sodium aluminate. In this form, alumina can be extracted from the spent shale waste by leaching with water or with dilute soda carbonate brine. Alumina may then be precipitated from the leachate. This method of obtaining alumina is attractive when compared with the more costly conventional method known as the Bayer process.

2.4.4 Sulfur and Nitrogen

Table 2.4-10 presents the distribution of sulfur and nitrogen in samples of mineable Colorado oil shale from the Mahogany zone [Stanfield, 1951]. Additional data on the distribution of sulfur

TABLE 2.4-10. AVERAGE DISTRIBUTION OF SULFUR AND NITROGEN IN OIL SHALE

	Weight percent	Remarks
Type of sulfur compound		
Sulfide sulfur	67	As pyrite and marcasite, FeS_2
Organic sulfur	33	
Sulfate sulfur	Trace	As $CaSO_4$, $FeSO_4$ and $MgSO_4$
Type of nitrogen compound		
Organic	100	No inorganic nitrogen found

Source: Stanfield, 1951

in various grades of oil shale were reported in the Annual Report of the Secretary of the Interior for 1949, Part II. These data appear in Table 2.4-11.

TABLE 2.4-11. DISTRIBUTION OF SULFUR AND NITROGEN IN COLORADO OIL SHALE

Oil yield of shale, gallons per ton	Total sulfur, weight percent	Total nitrogen, weight percent
10.5	0.62	0.28
26.7	0.56	0.54
36.3	0.73	0.44
57.1	1.96	-
61.8	1.99	0.66
75.0	1.86	-

Annual Report of the Seceretary of the Interior: Part II, 1949

2.4.5 Moisture

There is no consistent relationship between field moisture of oil shale and oil yield from shale. Typical values for field moisture varied from 0.38 to 2.93 percent [Stanfield, 1951].

A method for determining the moisture content of oil shale is presented in U.S. Bureau of Mines Report of Investigations No. 4477, which deals with the modified Fischer Assay method.

2.4.6 Trace Elements

The levels of selected trace elements in raw oil shale are shown in Table 2.4-12 [Poulson, et al., 1975]. Also shown in the table are representative mean values of the trace element contents [Denver Research Institute, 1977]. Gold assays were also made on 71 one-foot core samples representing the Mahogany ledge. The samples yielded an average of 0.00056 ounce of gold per ton [Stanfield, 1951].

TABLE 2.4-12. LEVELS OF TRACE ELEMENTS IN GREEN RIVER OIL SHALE

	Concentration as reported by Poulson, ppm		
Element	Mahogany zone	Saline zone	Concentration as reported by DRI, ppm
Be	2	1	1.3
Hg	0.5	-	0.4
Cd	0.1	0.4	1
Sb	0.4	3	1
Se	3.0	1.5	1.5
Mo	15	30	10
Ni	300	85	25
Pb	3	15	20
As	30	20	35
Cr	400	100	34
Cu	45	30	37
Zr	30	50	40
B	80	50	65
Zn	15	30	70
V	100	80	100
Mn	250	250	250
F	2000	1000	1000

Source: Poulson et al., 1975 and Denver Research Institute, 1977

Recent studies have confirmed the magnitude of the mercury content shown in Table 2.4-13 [Donnell, 1977]. Using flameless atomic absorption, an oil shale sample, which had previously been found to contain 4.0 ppm mercury, (USGS in 1959) was found to actually contain 0.35 ppm. Additional samples were tested an no relationship between oil content and mercury was apparent. It has been shown that the majority of the mercury present in oil shale ends up in the gaseous Fischer Assay products.

2.5 PHYSICAL PROPERTIES

2.5.1 Visual Features

The visual features of six specimens of Green River oil shale, selected so as to range in grade from 10 gallons per ton to 75 gallons per ton, are presented as Table 2.5-1 [Stanfield, 1951]. Shale of most interest would assay in the 15 to 30 gallon per ton range.

The color of fragments of Green River oil shale varies with the richness or organic content of the material. Rich shale appears dark in color due to the relative abundance of dark-colored organic matter (kerogen) present. The inorganic materials present, such as clays, carbonates, and silica, are generally light colored. Some rich shale is also light brown in color.

Easily visible in Green River oil shale are repetitive thin laminations, called varves. Each varve consists of thin bands, one light and one dark in color. These are minute seasonal pairs of lamina which average between 20 and 30 microns in thickness, a micron representing 1/1000 of a millimeter. The mineral dolomite predominates in the layer made darker in color by higher organic matter content. The mode of formation of the varves has been described [Smith, 1968]. In overall effect, the varves present a woodgrained effect, a feature which probably has a bearing on the naming of a persistently rich zone of oil shale as the "Mahogany" zone.

The Green River oil shale often separates along bedding planes to form slab-like fragments. When broken across bedding planes, the fracture is generally conchoidal. The laminated structure of oil shale has an important effect on measured physical properties of the rock, depending upon whether the direction of the examination is parallel with or perpendicular to the laminations. Lean shale has relatively uniform properties in both directions.

2.5.2 Specific Gravity

There exists a relationship between the organic (kerogen) content of oil shale and the specific gravity of oil shale. Since the organic component of oil shale has a specific gravity of about 1.1

TABLE 2.5-1. VISUAL FEATURES OF GREEN RIVER OIL SHALE

Sample grade, gal/ton	Color	Type of fracture	Type of laminations	Observed structure	Visible grains	Overall composition
10.5	Gray and brown	Conchoidal	Fine	Banded with dolomitic sandstone	None	Shale and sandstone banding
26.7	Gray and brown	Parallel to laminae	Fine	Dolomitic sandstone and folded shale laminae	Mica flakes	Sandy shale and sandstone
36.3	Dark brown	Parallel to laminae	Fine	Elongated concretions	Analcite	Sandy shale
57.1	Dark gray and brown	Parallel to laminae	Fine	Concretions and loop bedding	Calcite	Uniform shale
61.8	Dark gray and brown	Parallel to laminae	Fine	Platy and loop bedding	None	Uniform shale
75.0	Rich dark brown	Parallel to laminae	Fine	Platy and loop bedding	Calcite	Uniform shale

Source: Stanfield, 1951

and since the mineral components of oil shale have specific gravities ranging from 2.2 (for analcime) to 5.0 (for pyrite), an increase in the organic content of an oil shale causes a decrease in specific gravity of the oil shale.

The graph presented as Figure 2.5-1 displays average values for oil shale samples from the Anvil Points area in Colorado [Smith, 1956].

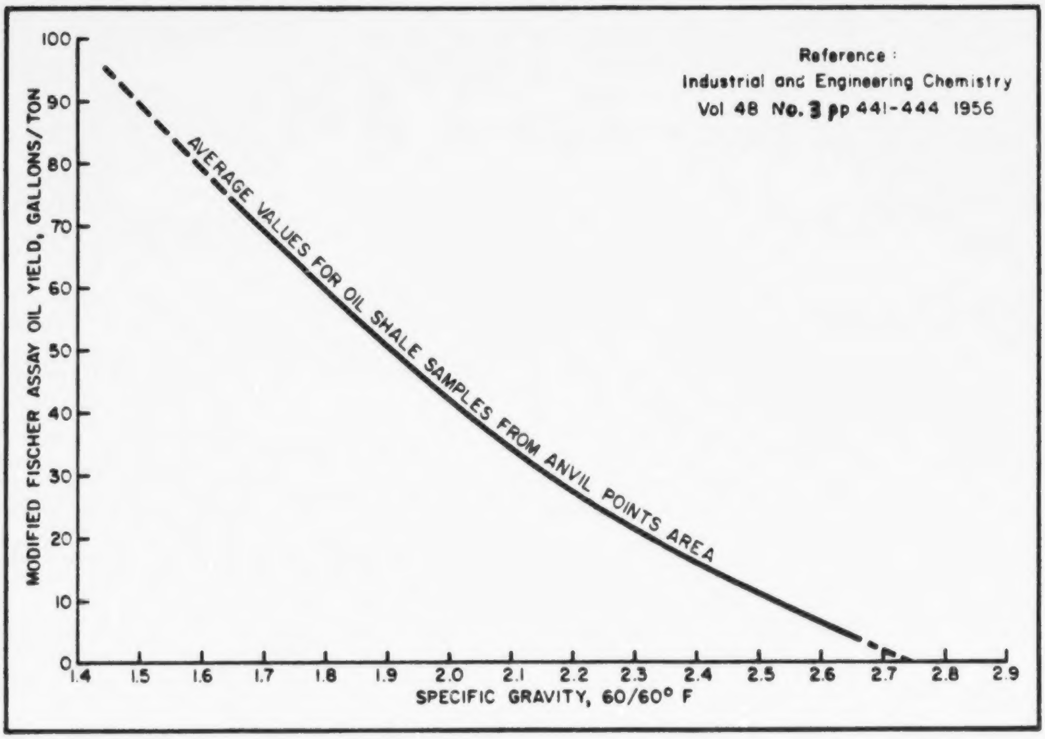


Figure 2.5-1. Specific Gravity and Oil Yield of Colorado Oil Shales. Source: Smith, 1956 (Reprinted with permission from I.&E.C. Copyright American Chemical Society.)

A basic equation for the relationship between organic content and oil shale density was developed [Smith, 1969]. The equation is:

$$D_T = \frac{D_A D_B}{A(D_B - D_A) + D_A}$$

D_T = Shale density
A = Weight fraction of organic matter
B = Weight fraction of mineral matter
D_A = Average density of organic fraction, (g/cm^3)
D_B = Average density of mineral fraction, (g/cm^3)

Plotted values agree closely with those shown on Figure 2.5-1, when values in the range of natural occurrence in oil shales are assigned to D_B(2.7 g/cm^3) and D_A(1.05 g/cm^3).

Taking the specific gravity/organic content correlation one step further, an empirical relationship between specific gravity and oil yield in gallons per ton, as determined by the Fischer Assay method was also developed [Smith, 1956]. This relationship is expressed by:

$$Y = 31.563 X^2 - 205.998 X + 326.624$$

Where Y = oil yield in gallons per ton
X = specific gravity of Green River oil shale at 60/60°F.

In another study an equation relating the oil yield of New Albany shale to specific gravity was developed [Smith et al., 1964]. This relation is as follows:

$$Y = 93.482 - 34.355 X$$

Where Y = oil yield in gallons per ton
X = specific gravity of New Albany oil shale

The calculated relationships between grade, specific gravity, weight (in place) and weight (broken 38 percent voids) for typical Green River formation oil shale are presented in Table 2.5-2.

2.5.3 Porosity and Permeability

The porosity of Green River oil shale before and after heating has been reported [Dinneen, 1972]. The data were obtained on samples ranging in grade from 1.0 to 60 gallons per ton. These shales were heated under controlled conditions to 950°F to remove the organic matter and further heated to 1500°F to decompose the mineral carbonates. During the thermal treatment, the oil shale samples were in a stress-free environment. Table 2.5-3 presents the measurable porosities of the raw and treated oil shale samples.

TABLE 2.5-2. WEIGHT (INPLACE) AND WEIGHT (BROKEN) FOR GREEN RIVER OIL SHALE

Shale grade, gal/ton	Spec. grav.	Weight, in place			Weight broken, 38% voids		
		lbs/ft^3	ft^3/ton	tons/yd^3	lbs/ft^3	ft^3/ton	tons/yd^3
0	2.714	169.1	11.8	2.28	105	19	1.42
15	2.383	148.5	13.5	2.00	92	22	1.2
25	2.218	138.2	14.5	1.86	86	23	1.2
30	2.145	133.6	15.0	1.80	83	24	1.1
35	2.076	129.3	15.5	1.74	80	25	1.1
40	2.012	125.3	16.0	1.69	78	26	1.0

Source: Baughman, 1978

TABLE 2.5-3. POROSITIES OF RAW AND THERMALLY TREATED OIL SHALES (PERCENT OF BULK VOLUMES)

Oil yield, liters per metric ton	Measurable porosity of raw oil shale	Porosity after heating to 510°C (950°F)	Porosity after heating to 816°C (1500°F)
4.2	10.54	13.36	24.83
27.1	5.53	14.70	20.89
56.3	0.57	19.09	32.03
1104.3	0.30	30.41	53.85
125.2	0.14	36.34	51.90
164.8	0.16	45.35	62.91
244.1	0.13	61.16	70.69

Source: Dinneen, 1972

The mineral matrices of the oil shales yielding less than about 9.6 gallons of oil per ton did not undergo noticeable structural breakdown upon heating to 950°F. For richer shales, the structural breakdown becomes more noticeable as the grade of shale increases, so that for shales yielding more than 30 gallons per ton, there is extensive fracturing and swelling.

The effect of heat, stress, and time on permeability of test columns of Green River oil shale samples of various grades were determined [Tisot et al., 1971]. As compressive strain increased with time, the columns' pre-geometry, porosity, and permeability were concurrently undergoing change. Permeability was expressed as the amount of nitrogen (STP) which passed through the column of fragments (in cubic inches per square inch of cross-sectional area per minute).

2.5.4 Mechanical Properties

2.5.4.1 Shear Strength

Shear strengths of lean oil shale samples cut from the roof material in the experimental underground oil shale mine of the U.S. Bureau of Mines at Anvil Points, Colorado, are presented in Table 2.5-4 [Agapito, 1972].

2.5.4.2 Compressive Strength

The compressive strengths of core samples of Green River oil shale before and after thermal treatment have been reported [Dinneen, 1968 and 1972]. The untreated samples displayed high compressive strength values that were about the same, whether determined perpendicular to or parallel to the bedding planes of the shale.

TABLE 2.5-4. SHEAR STRENGTHS OF LEAN OIL SHALE SPECIMENS FROM ROOF MATERIAL OF USBM EXPERIMENTAL MINE (ANVIL POINTS)

Direction of shearing force to the bedding planes	Shear strength, lb/sq. in.	Number of samples tested	Standard deviation (percent)
Perpendicular	3,490	5	4.9
Perpendicular	4,640	5	3.1
Parallel	1,770	5	10.5
Perpendicular	3,560	5	5.1
Perpendicular	3,145	5	6.0
Parallel	890	5	8.3
Perpendicular	3,205	5	5.2
Parallel	920	5	9.1

Source: Agapito, 1972

After heating to 950°F, the lean shales retained high compressive strength values in both horizontal and vertical planes, indicating a high degree of inorganic cementation between the mineral particles comprising each lamina and between adjacent laminae. Dinneen showed the compressive strength of rich shale is quite low after removal of the organic matter. Decomposition of the mineral carbonates at 1500°F apparently does not greatly affect the compressive strength. The results are presented in Table 2.5-5, expressed in metric system units [Dinneen, 1968 and 1972]. English system unit may be derived from Figure 2.5-2.

A rather comprehensive report on the compressive strength of roof and mine support pillar specimens cut perpendicular to bedding planes was prepared [Agapito, 1972]. The specimens were obtained in the room-and-pillar system underground shale mine of Mobil Oil Company, near Anvil Points, Colorado. The data are summarized in Table 2.5-6.

That the compressive strength of oil shale varies with the grade of the shale is presented in Figure 2.5-3 [Sellers, 1971].

2.5.4.3 Hardness

For two Green River core samples tested, the hardness of the horizontal core was 61 (scleroscope hardness number) and for the vertical core was 55 [Matzick et al., 1956].

2.5.5 Leachate Quality and Quantity

The modified *in-situ* method of oil shale retorting and the various surface methods require that quantities of raw (unretorted) shale

TABLE 2.5-5. COMPRESSIVE STRENGTHS OF RAW AND THERMALLY-TREATED OIL SHALES (KILOGRAMS PER SQUARE CENTIMETER)

Oil yield, liters/metric ton	Raw oil shales		Oil shale heated to 510°C		Oil shale heated to 816°C	
	A[a]	B[b]	A	B	A	B
4.2	1,560	1,364	1,406	1,343	1,090	1,048
27.1	2,194	1,997	1,983	1,842	1,202	956
56.3	1,870	1,645	935	436	738	260
104.3	1,294	1,308	29	27	12	11
125.2	696	745	25	20	8	8
164.8	809	969	5	8	6	8
244.1	914	907	2	2	4	2

[a] Compressive strength perpendicular to the bedding planes.

[b] Compressive strength parallel with the bedding planes.

Source: Dinneen, 1968 and 1972

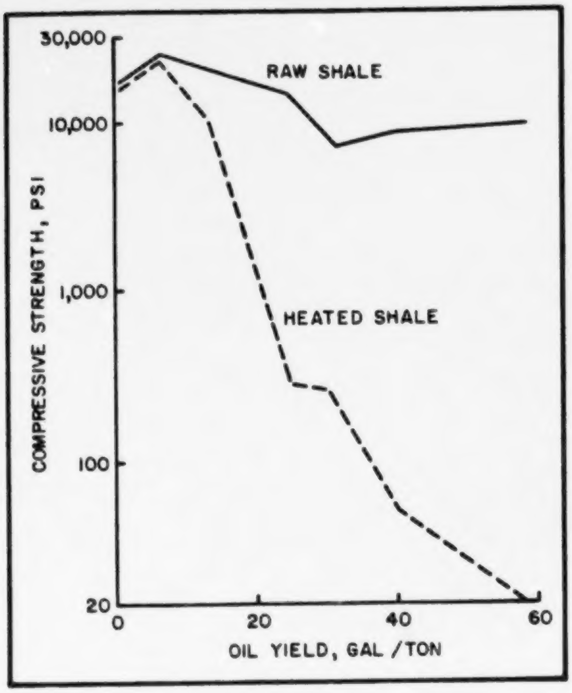


Figure 2.5-2. Compressive Strength of Oil Shales. Source: Dinneen, 1968 and 1972 (Reproduced with permission.)

be mined from shafts and drifts that provide access to the retorts. Raw shale is also mined to provide a void space into which the shale in the retort expands upon rubblization by blasting. The mined shale may be stored on the ground surface for a period of at least a few years and possibly even permanently. Underground mining and surface retorting will also require large storage piles of raw, mined shale for retort feed material. In addition lean shale and rejected raw shale fines may be permanently disposed. The placement of the raw mined shale on the surface places it in an environment with which it is no longer in geochemical equilibrium. Subsequent precipitation on the pile creates the potential for the release of leachate containing a variety of chemicals into percolating waters at elevated levels relative to the base line conditions.

A reconnaisance study of leachate quality from raw mined oil shale with emphasis on shale from Federal lease tracts C-a and C-b has been reported [EPA-600/7-80-181, 1980]. The study employed laboratory leaching columns containing a variety of samples of raw shale and soils which were obtained from the Piceance Basin of Colorado. The purpose of extending the study to selected soil samples was to provide a background and perspective from which to view raw shale leachate properties. Included were four raw

TABLE 2.5-6. COMPRESSIVE STRENGTH OF GREEN RIVER OIL SHALE SAMPLES CUT PERPENDICULAR TO BEDDING (SAMPLES FROM USBM EXPERIMENTAL MINE, ANVIL POINTS, COLORADO)

Distance from Mahogany marker, feet	Bed designation[a]	Number of specimens tested	Compressive strength, psi
31.6 above	Roof	2	15,380
21.5-26.8 above	do	2	14,890
20 above	do	3	12,430
18.5 above	A	1	17,100
10 above	B	2	15,000
4.2 above	C	1	17,100
2.5 below	D	1	19,000
4.5 below	D	2	12,650
7 below	D	2	11,730
10 below	D	1	10,700
12.5 below	E	1	12,520
14 below	E	3	8,280
14.6 below	E	5	7,350
15.5 below	F	3	11,910
17 below	F	1	12,080
17.5 below	F	1	9,190
18.5 below	F	8	8,160
20 below	G	1	14,480
20.5 below	G	1	14,470
23 below	G	2	10,250
23 below	G	2	8,600
26.6 below	G	2	14,090
27 below	G	3	12,960
31 below	H	3	8,560
33 below	H	1	13,600
37 below	H	1	15,390
39.5 below	H	2	17,280
46.5 below	I	2	12,700

[a] Designations refer to arbitrarily-designated groups of mineable beds, lettered A through I.
Source: Agapito, 1972

shales, two soils, one sample of naturally leached outcropping shale, and one sample of naturally retorted shale from a surface fire of unknown age.

Leaching was conducted by passing deionized water through columns of each material. Both saturated and unsaturated tests were conducted. Samples of the effluents were collected and subjected to chemical analyses. The ranges of concentration variation observed

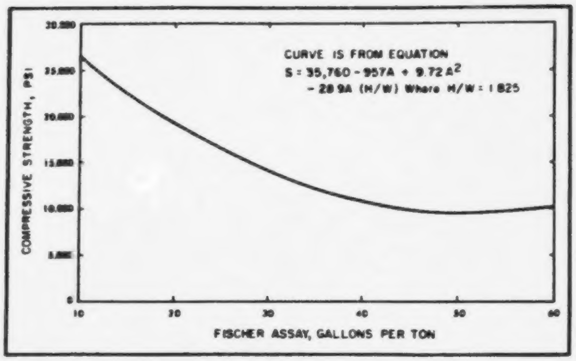


Figure 2.5-3. Compressive Strength versus Fischer Assay of Colorado Oil Shale, Anvil Points Mine. Source: Sellers, 1971

in leachates from each of the materials tested are presented in Table 2.5-7. It was found that the leachate contained dissolved solids at elevated concentrations relative to the background. The major contributors to the dissolved solids content are calcium, magnesium, sodium, bicarbonate, chloride and sulfate. A comparison of trace element concentrations in the leachates is presented in Table 2.5-8. The concentrations of four elements of potential toxicological significance: Al, B, F, and Zn were found to be significantly greater in the leachates from some of the mined shales than in the corresponding samples from the previously exposed materials. The levels of all other trace elements produced by the mined shales were comparable to those observed from the soils and previously exposed shales.

From comparisons of the maximum observed concentrations of various parameters with drinking water criteria, it was concluded that even the worst leachate from the columns did not exceed 100 times drinking water standards for measured parameters. However, the maximum concentrations of Cr, F, Fe, Hg, Mn, NO_3, Pb, SO_4, TDS, and Zn were found to exceed drinking water criteria.

As a result of the laboratory study [EPA-600/7-80-181, 1980], a cooperative field study was initiated and reported [EPA-600/D-84-143, 1984]. In this study the quantity and quality of leachate generated under field conditions for storage piles of raw mined oil shale was investigated for storage piles ranging from 5 to 20 feet in depth. Leachate collection systems were installed on Federal lease tracts C-a and C-b in Colorado and the quantity and quality of the leachates were recorded over nearly a 3 year period from 1981 to 1983.

The mean concentrations of the major ionic species found in the leachates from the C-a and C-b tracts are presented in Table 2.5-9 and 2.5-10. In the case of the C-a tract, the leachate from the

TABLE 2.5.7. SUMMARY OF THE RANGE OF CONCENTRATIONS IN LEACHATE SAMPLES

Parameter	Units	USBM raw shale	Colony raw shale	C-a R-5/ Mahog. shale	C-a composite	Colony Nat. leached	Union Nat. retorted	Colony soil	C-b soil	Drinking water criteria
Al	mg/L	0.34-7.54	<0.05-0.75	0.3-3.53	<0.05-0.69	<0.05-0.17	<0.05-0.1	<0.05-0.37	<0.05	-
As	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.05
B	mg/L	0.24-43	<0.025-2.75	<0.025-0.59	<0.025-1.97	0.12-0.365	0.165-0.39	0.47-0.76	0.65-0.985	-
Ba	mg/L	0.061-0.17	0.07-0.48	0.088-0.27	0.027-0.22	0.088-0.495	0.028-0.35	0.12-0.57	0.038-0.240	1.0
Be	mg/L	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	-
Ca	mg/L	36-750	40-1550	180-1510	18-970	25-500	10-49	40-960	6.5-330	-
Cl	mg/L	<1.0-560	1.1-22	1.9-300	0.3-130	0.8-71	1.1-15	0.1-200	1.8-520	-
CO_3	mg/L	0.1-1.1	0.03-1.6	<0.1-346	0.3-0.7	0.12-1.03	<1.0-22	0.17-2.9	1.0-8.8	-
Cr	mg/L	<0.025-0.68	<0.025-0.04	0.022-0.034	<0.025-0.043	<0.025	<0.025-0.71	<0.025	<0.025-0.069	0.05
Cu	mg/L	<0.025-0.30	<0.025-0.41	<0.025-0.69	<0.025-0.44	<0.039-0.31	<0.025-0.33	0.075-0.38	<0.025-0.28	1.0
EC	µmhos/cm	280-13000	240-5400	1900-37000	125-8200	240-4200	300-1300	370-9000	840-3000	-
F	mg/L	9.5-75	4.0-7.2	0.8-65	<0.5-3.0	4.0-8.7	5.4-6.6	1.2-10	4.5-25	1.8
Fe	mg/L	0.01-1.8	<0.03-0.89	<0.1	<0.1	<0.03-0.08	<0.05	<0.01-0.52	0.1-0.42	0.3
HCO_3	mg/L	83.1-321	50-558	3.0-403	82-1026	136-233	168-585	152-480	481-846	-
Hg	mg/L	<0.0001-0.0035	<0.0005	<0.0001	<0.0001	<0.0005	<0.0001	<0.0005	<0.0001	0.002
K	mg/L	1.1-22	1.7-59	8.2-640	0.4-34	0.83-57	9.2-74	25-270	1.3-22	-
Li	mg/L	0.02-3.1	0.02-0.151	0.02-0.11	<0.02-0.79	<0.004-0.02	0.14-0.51	0.03-0.47	0.02-0.08	-
Mg	mg/L	6.7-1050	5.5-140	0.675-108	4.9-820	17-365	30-108	17-1450	2.6-145	-
Mn	mg/L	0.075-3.2	0.074-2.74	<0.05-0.35	<0.05-0.40	<0.05-0.11	<0.05	<0.05-0.97	<0.05-0.16	0.05
MO	mg/L	0.09-0.87	0.09-0.65	0.10-5.18	0.10-2.2	0.075-0.74	0.065-0.45	<0.05-0.84	<0.05-0.43	-
Na	mg/L	<25-1430	5.8-145	27-7710	4.3-1240	14-350	12-75	3.8-340	210-2050	-
Ni	mg/L	<0.025-0.60	<0.05-0.10	0.047-0.085	<0.05-0.16	<0.05-0.06	<0.05	<0.05-0.07	<0.05-0.075	-
NO_3	mg/L	<1.25-40	0.9-25	4-172	<0.5-140	<0.3-245	0.5-8	<0.2-180	1.4-30	10
Pb	mg/L	<0.04-1.9	<0.05-0.64	<0.05-0.83	<0.05-0.77	0.12-0.35	0.05-0.16	0.12-0.38	0.07-0.31	0.05
pH	-	6.8-8.06	7.06-8.18	6.93-11.98	7.03-7.99	6.93-8.11	7.20-8.81	7.1-8.2	7.43-8.49	-
Se	mg/L	<0.01	<0.01	<0.005	<0.005	<0.01	<0.005	<0.01	<0.005	0.01
Si	mg/L	1.65-9.7	2.12-10.58	1.2-23.28	5.8-19.58	6.71-14.72	8.8-19.06	8.0-16.8	11.0-20.7	-
Sn	mg/L	<0.025-1.28	0.12-0.67	-	-	0.041-0.67	-	<0.025-1.37	-	-
SO	mg/L	20-5700	28-5150	5-6600	7.9-6100	15-2650	9-128	60-4200	23-860	250
TDS	mg/L	70-13300	110-7160	610-30130	164-9450	120-4760	460-1200	250-7450	1050-3760	500
Zn	mg/L	0.01-6.8	<0.02-0.68	<0.01-0.09	<0.02-1.5	0.07-0.3	0.02-0.15	0.01-0.65	0.04-0.35	5.0

Source: EPA-600/7-80-181, 1980

TABLE 2.5-8. COMPARISON OF TRACE ELEMENT CONCENTRATIONS FROM RAW MINED SHALE WITH THOSE FROM SOILS AND PREVIOUSLY EXPOSED SHALES

	Raw mined shales		Soils and previously exposed shales		
Element	Maximum concentration observed, mg/L	Test yielding maximum concentration	Maximum concentration observed, mg/L	Test yielding maximum concentration	Drinking water criteria
Al	7.54	USBM, unsaturated	0.37	Colony soil	-
As	<0.005	--	<0.005	--	0.05
B	43	USBM, #2 saturated	0.99	C-b soil	-
Ba	0.48	Colony raw, #2 sat.	0.50	Colony nat.	1.0
Be	0.025	--	<0.025	--	-
Cr	0.68	USBM, #1 saturated	0.71	Union nat. ret.	0.05
Cu	0.69	C-a R-5/Mahog., unsat.	0.38	Colony soil	1.0
F	75	USBM, #1 saturated	25	C-b soil	1.8
Fe	1.8	USBM, #1 resaturated	0.52	Colony soil	0.30
Hg	0.0035	USBM, #2 saturated	<0.0005	--	0.002
Li	3.1	USBM, #2 saturated	0.51	Union nat. ret.	-
Mn	3.2	USBM, #2 saturated	0.97	Colony soil	0.05
Mo	5.18	C-a R-5/Mahog., unsat.	0.84	Colony soil	-
Ni	0.60	USBM, #2 saturated	0.075	C-b soil	-
Pb	1.9	USBM, #1 saturated	0.38	Colony soil	0.05
Se	<0.01	--	<0.01	--	0.01
Si	23.28	C-a R-5/Mahog., unsat.	20.7	C-b soil	-
Sn	1.28	USBM, #2 saturated	1.37	Colony soil	-
Zn	6.8	USBM, #1 saturated	0.65	Colony soil	5.0

Source: EPA-600/7-80-181, 1980

TABLE 2.5-9. MEAN VALUES FOR MAJOR ION COMPOSITION OF C-a LEACHATE

Collector/ year	Mg/L								
	Ca	Mg	Na	K	SO_4	Cl	HCO_3	NO_3	TDS
5 ft/1981	31.6	369.3	38.2	0.2	427.1	4.6	6.3	28.6	30,080
15 ft/1981	28.0	637.3	54.7	0.2	738.5	10.3	5.3	30.2	53,350
5 ft/1982	20.1	253.5	24.1	0.1	431.7	5.0	5.2	21.2	28,840

Source: EPA-600/D-84-143, 1984

TABLE 2.5-10. MEAN VALUES FOR MAJOR ION COMPOSITION OF C-b LEACHATE

Collector/ year	Mg/L								
	Ca	Mg	Na	K	SO_4	Cl	HCO_3	NO_3	TDS
10 ft/1981	22.5	17.9	45.4	0.2	76.7	0.4	2.9	2.5	6,450
15 ft/1981	22.9	20.9	47.6	0.1	83.5	0.3	2.9	1.8	7,050
20 ft/1981	22.8	19.2	43.5	0.1	76.6	0.7	2.3	2.7	6,510
10 ft/1982	21.6	28.2	47.8	0.2	85.4	0.4	2.9	0.7	7,080
15 ft/1982	18.9	33.5	51.8	0.2	94.9	0.5	2.6	1.1	7,600
20 ft/1982	21.6	23.0	45.1	0.1	80.3	0.5	2.2	1.9	6,470

Source: EPA-600/D-84-143, 1984

raw shale was highly saline with a mean concentration of dissolved solids of 29,500 mg/L for the 5 ft. depth pile and 60,220 mg/L for the 15 ft. depth pile. These waters were found to be a magnesium-sulfate type, with these two constituents accounting for 87% of the total equivalent weight of the dissolved solids. The pH ranged from 6.9 to 7.9 throughout the study.

In the case of the C-b tract the quantity of dissolved solids in the leachate was lower; averaging 6,850 mg/L and the pH ranged from 7.4 to 8.4. The composition of the C-b leachate is dominated by sodium and sulfate, rather than magnesium and sulfate exhibited in the C-a leachate. In both cases it appeared that the calcium concentration was controlled by the solubility of calcium sulfate.

The mean values of trace element concentrations in the C-a and C-b tract leachates are presented in Tables 2.5-11 and 2.5-12. The data are averaged over two years of sampling for various pile depths. The concentrations of fluoride observed in the field generated leachates were similar to those measured in the previous laboratory column leaching study [EPA-600/7-80-181, 1980], even though the shale samples differed. The concentrations of zinc, boron, and aluminum found in the field study were significantly less than the maximum values observed in the laboratory column studies (compare Tables 2.5-11 and 2.5-12 with Table 2.5-8). The differences may be due to the difference in materials used in the two studies. The maximum values of the species analyzed in the field study are presented in Table 2.5-13. Although the concentrations of many trace elements were sometimes observed to be greater than various recommended maxima for particular uses (e.g., drinking water), the large concentrations of the common species is more likely to be the significant quality characteristic of these leachates.

The cumulative volume of leachate per unit area measured over nearly three years at the C-a tract ranged from 6.26 to 13.72 cm per year. These volumes represent 7 and 16 percent, respectively, of the incident precipitation over the same time period. The larger value is believed to be more representative of the actual leachate volume generated in the pile. The cumulative volume of leachate at the C-b tract ranged from 11.52 to 17.02 cm per year. These volumes represent 12 and 17 percent, respectively, of the incident precipitation over the same time period. Leachate volumes of these magnitudes are believed to be larger than the natural recharge rates on undisturbed lands receiving similar volumes of precipitation. The raw shale piles were formed from mine-run size material and remained unvegetated. Therefore, infiltration capacity was high and both evapotranspiration and direct runoff capacity were low.

TABLE 2.5-11. MEAN VALUES OF TRACE ELEMENT CONCENTRATIONS OF C-a LEACHATE

Collector/ year	Mg/L								
	F	Zn	B	Si	Mo	Mn	Ni	Al	Sr
5 ft/1981	10.4	0.24	0.46	3.7	<0.05	2.0	0.36	0.35	6.1
15 ft/1981	17.0	0.18	0.46	2.3	<0.05	1.8	0.32	0.21	8.4
5 ft/1982	21.3	0.16	0.48	4.4	0.53	0.73	0.34	2.01	6.5
15 ft/1982	30.1	0.23	1.07	4.8	0.35	1.3	0.57	1.54	10.0

Source: EPA-600/D-84-143, 1984

TABLE 2.5-12. MEAN VALUES OF TRACE ELEMENT CONCENTRATIONS OF C-b LEACHATE

Collector/ year	Mg/L								
	F	Zn	B	Si	Mo	Mn	Ni	Al	Sr
10 ft/1981	7.75	0.19	0.53	4.8	3.9	0.14	0.20	1.33	9.0
15 ft/1981	8.35	0.25	0.51	4.4	2.5	0.16	0.15	0.87	9.0
20 ft/1981	7.24	0.17	0.38	3.6	1.6	0.11	0.21	0.49	9.1
10 ft/1982	5.50	0.06	0.77	7.6	0.93	0.19	0.03	1.12	6.5
15 ft/1982	6.81	0.19	0.76	3.9	0.88	0.08	0.06	1.25	5.8
20 ft/1982	5.11	0.70	0.70	3.1	0.94	0.21	0.05	1.23	7.7

Source: EPA-600/D-84-143, 1984

TABLE 2.5-13. MAXIMUM OBSERVED CONCENTRATIONS IN RAW SHALE LEACHATES

Species	Concentration, mg/L	Location	Date
HCO_3	579	C-a, 15 ft	9/21/82
CO_3	5.68	C-a, 15 ft	7/19/82
TDS	72,660	C-a, 15 ft	8/16/82
F	113	C-a, 15 ft	7/26/82
Cl	366	C-a, 15 ft	7/01/82
PO_4	0.28	C-b, 20 ft	2/25/82
NO_3	2,564	C-a, 15 ft	7/26/82
SO_4	45,900	C-a, 15 ft	5/10/82
Zn	0.597	C-a, 15 ft	8/16/82
Fe	2.02	C-a, 15 ft	8/11/82
Co	1.17	C-a, 15 ft	8/23/82
Li	0.339	C-b, 10 ft	7/26/82
NH_3	2.55	C-a, 5 ft	8/30/82
B	1.97	C-b, 15 ft	7/26/82
Cd	0.168	C-a, 15 ft	7/26/82
Be	0.300	C-b, 10 ft	7/06/82
Mg	12,830	C-a, 15 ft	9/06/82
P	7.0	C-a, 15 ft	8/04/82
Si	13.2	C-a, 15 ft	6/02/82
Mo	1.5	C-b, 10 ft	7/06/82
Mn	2.34	C-a, 15 ft	6/02/82
Ni	1.12	C-a, 15 ft	6/02/82
Na	2,030	C-a, 15 ft	8/02/82
Cu	0.073	C-b, 10 ft	7/06/82
Al	5.28	C-a, 5 ft	7/01/82
Ca	505	C-a, 15 ft	3/22/82
Ba	0.822	C-b, 10 ft	9/23/82
K	16.4	C-a, 15 ft	7/19/82
Cr	0.290	C-a, 15 ft	6/02/82
Sr	15.4	C-a, 15 ft	7/19/82
Pb	1.036	C-a, 15 ft	8/11/82
Ag	0.012	C-a, 15 ft	3/17/82
Ti	0.007	C-a, 15 ft	4/12/82
Se	0.013	C-a, 15 ft	7/01/82
As	0.007	C-b, 20 ft	8/04/82
Hg	0.003	C-b, 20 ft	2/25/82

Source: EPA-600/D-84-143, 1984

SECTION 3

SOLID WASTES AND THEIR CHARACTERISTICS FOR OIL SHALE RETORTING PROCESSES

3.1 LURGI-RUHRGAS OIL SHALE RETORTING

3.1.1 Retorting Operation

A schematic for the Lurgi retorting process [EPA-600/8-83-005, 1983] is shown in Figure 3.1-1. Initial crushing in the pit reduces the size of the run-of-mine shale to minus 8 inches. Secondary and tertiary crushing further reduce the shale size to minus 1/4 to 1/3 inches. The crushed oil shale is fed through a feed hopper to a double screw mixer, where four to eight times its weight of a hot (1,200-1,300°F) circulating heat carrier, such as sand or processed shale from the collecting bin, is thoroughly mixed in, thus heating the entire mixture to approximately 950-1,000°F within a few seconds. At this temperature, pyrolysis of the kerogen in the oil shale occurs, resulting in the production of retort gas, shale oil vapor and water vapor.

The circulating heat carrier and the partially retorted shale are then dropped from the screw mixer into the surge vessel, where residual oil components are distilled off. The mixture of heat carrier and retorted shale residue is passed to the lower section of the lift pipe, where combustion air (preheated to 450-900°F) is introduced, raising the mixture pneumatically to the collecting bin. Essentially all available organic carbon contained in the retorted shale residue is burned in the lift pipe. Supplemental fuel may be added to the bottom of the lift pipe to sustain the combustion of the organic residue when processing leaner oil shales. Also, at the high lift pipe temperature, a moderate amount of carbonate decomposition occurs in the processed shale.

At the top of the lift pipe, the hot, burned shale is separated from the flue gases in the collecting bin. Fines are carried out of the collecting bin with the flue gas stream. The coarse-grained shale residue accumulates in the lower section of the collecting bin and flows continuously to the mixer. Partial removal of the solids to prevent accumulation in the collecting bin may be required if the fines carry-over is not sufficient. The combustion air supplied to the lift pipe is preheated by counter-current heat exchange with the flue gas stream in the preheat section of the waste heat boiler. The calcined minerals

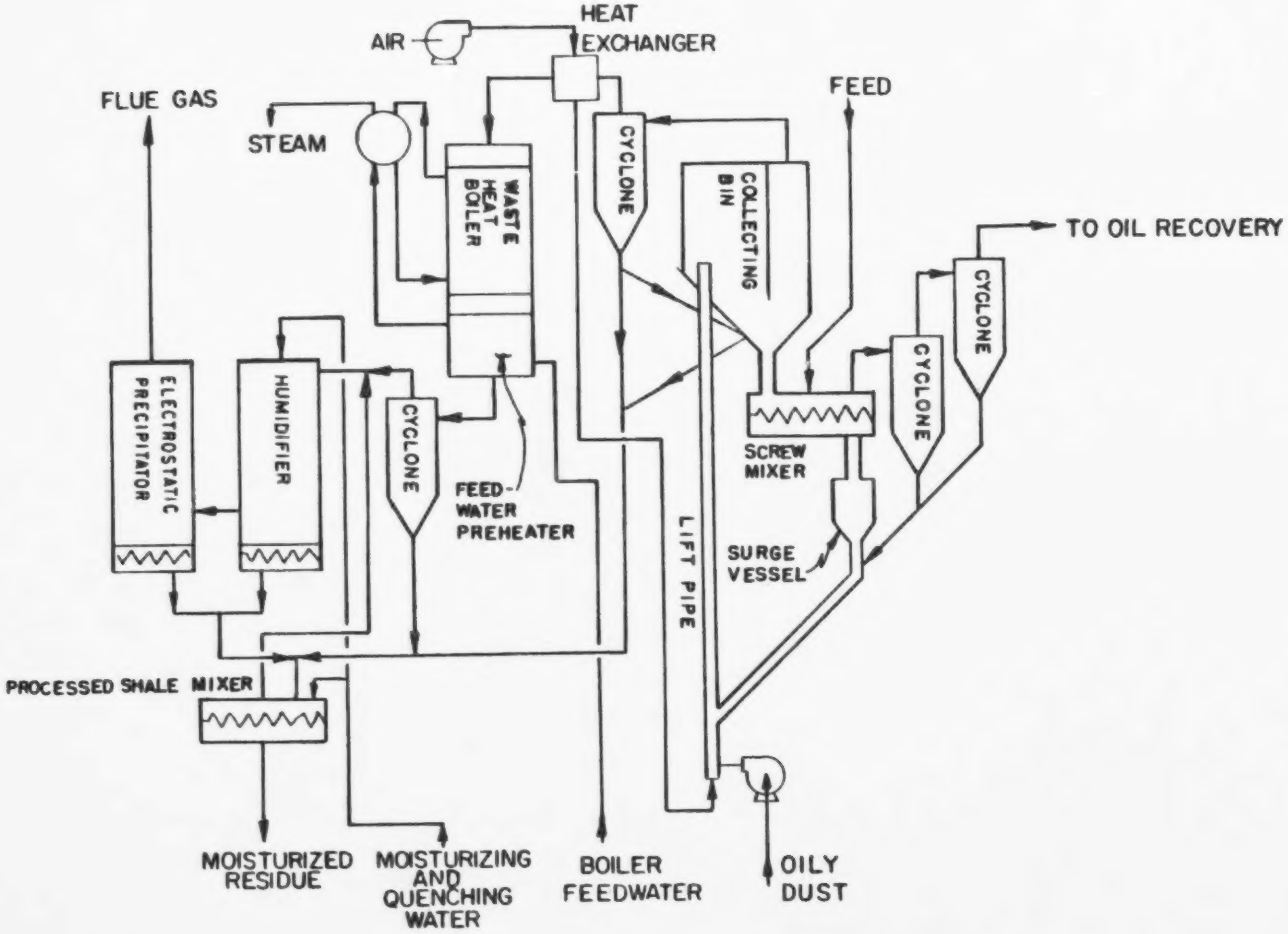

AIR
HEAT EXCHANGER
FLUE GAS
STEAM
FEED
WASTE HEAT BOILER
CYCLONE
COLLECTING BIN
TO OIL RECOVERY
CYCLONE
CYCLONE
ELECTROSTATIC PRECIPITATOR
HUMIDIFIER
CYCLONE
SCREW MIXER
FEED-WATER PREHEATER
LIFT PIPE
SURGE VESSEL
PROCESSED SHALE MIXER
MOISTURIZED RESIDUE
MOISTURIZING AND QUENCHING WATER
BOILER FEEDWATER
OILY DUST

Figure 3.1-1. Lurgi-Ruhrgas oil shale retorting process.
Source: EPA-600/8-83-005, 1983

in the burned shale combine with the sulfur dioxide produced by combustion of the organic sulfur to form calcium and magnesium sulfites and sulfates.

The pyrolysis products stream containing shale fines is withdrawn at the end of the screw mixer and passed through two series-connected cyclones to a product recovery section. The fines are separated in these cyclones and returned to the recycle system. The vapor stream then passes through a sequence of three scrubbing coolers (not shown). The first scrubbing cooler removes dust from the gas stream by condensation of heavier oil fractions. A dusty heavy oil is obtained at this point. In the next scrubbing cooler, further condensation of the oil takes place at a temperature above the dew point of water to produce a water-free middle oil. Final cooling of the gas produces an aqueous gas condensate and a light oil fraction. The light oil is separated from the condensate or gas liquor in an oil/water separator. Finally, the gas is scrubbed with a lean oil in the naphtha scrubber to recover naphtha and noncondensable gases, as deemed desirable.

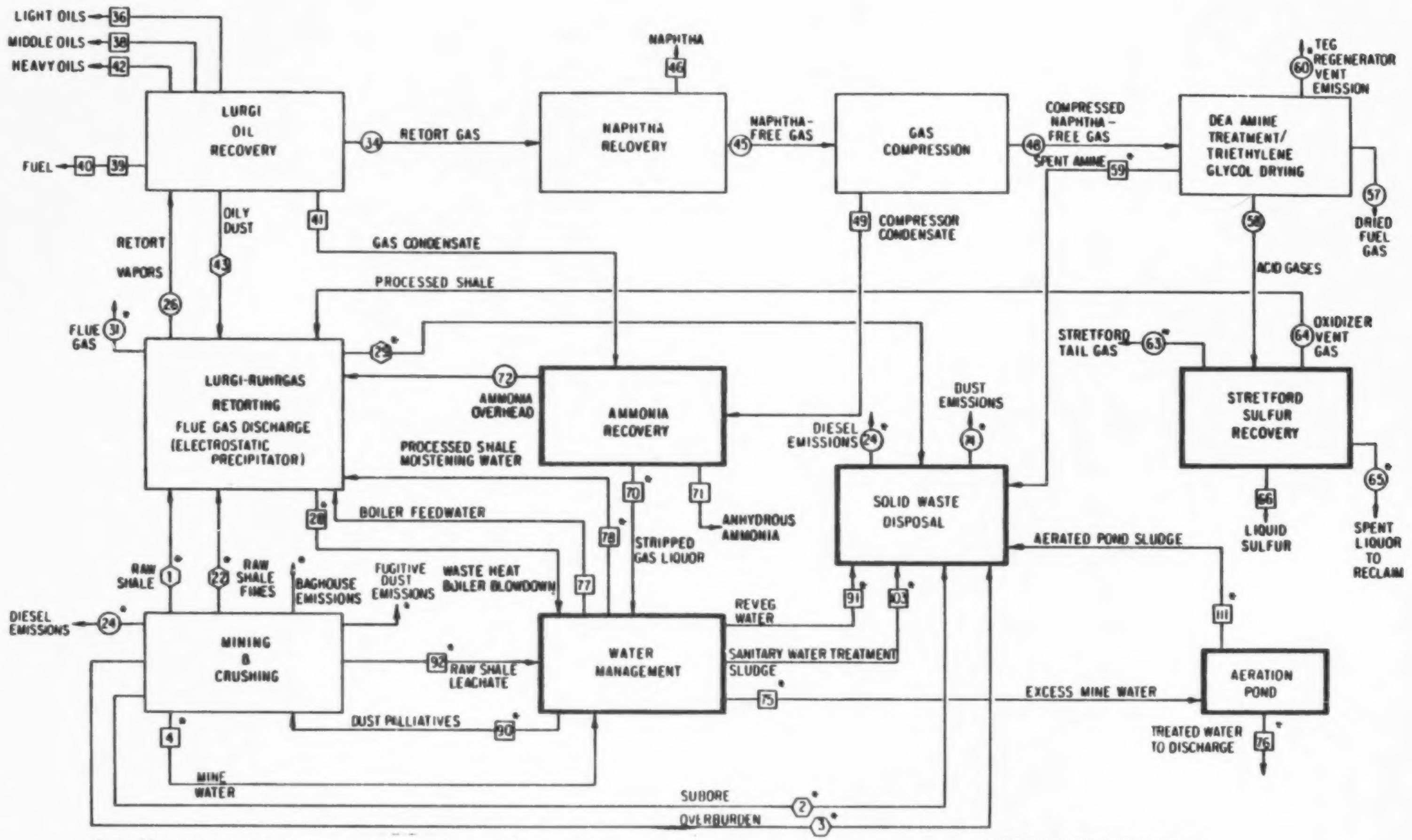
The flue gas stream in the lift pipe is dedusted in a cyclone after leaving the collecting bin; the dust is routed to the processed shale mixer. The gas stream is then routed through a heat exchanger for preheating of combustion air, a waste heat boiler to produce process steam, another cyclone, and a humidifier or flue gas conditioner. Additional dust removed by the waste heat boiler and cyclone are routed to the processed shale mixer. The flue gas stream is cooled somewhat and conditioned in the humidifier by adding steam generated during processed shale quenching. After humidification and cooling, residual dust is removed from the flue gas stream using an electrostatic precipitator and discharged into a processed shale quencher/moisturizer where more water is added to cool the solids. The processed shale residue, cooled to ~200°F, is moisturized to a suitable moisture content and discarded as open pit backfill.

3.1.2 Solid Wastes

A block flow diagram for the basic processing and pollution control system for the Lurgi process is presented in Figure 3.1-2.

In the retort off-gas discharge system, the flue gas and entrained processed shale particles are separated from each other via a series of cyclones, waste heat recovery system, humidifier, etc. The flue gas is then passed through an electrostatic precipitator to remove the residual particulates and is eventually vented to the atmosphere. The processed shale particulates separated along these steps is sent to the processed shale mixer for quenching and proper moisturizing before final disposal.

The retort gas is cleaned for marketing. The gas is first compressed to remove much of the moisture and ammonia, then subjected


LIGHT OILS
36
MIDDLE OILS
38
HEAVY OILS
42
FUEL
40
39
LURGI OIL RECOVERY
34
RETORT GAS
NAPHTHA
46
NAPHTHA RELOVERY
45
NAPHTHA-FREE GAS
GAS COMPRESSION
48
COMPRESSED NAPHTHA-FREE GAS
SPENT AMINE
59
60
TEG REGENERATOR VENT EMISSION
DEA AMINE TREATMENT/ TRIETHYLENE GLYCOL DRYING
57
DRIED FUEL GAS
58
ACID GASES
OILY DUST
43
41
GAS CONDENSATE
49
COMPRESSOR CONDENSATE
RETORT VAPORS
26
PROCESSED SHALE
FLUE GAS
31
29
LURGI-RUHRGAS RETORTING FLUE GAS DISCHARGE (ELECTROSTATIC PRECIPITATOR)
72
AMMONIA OVERHEAD
AMMONIA RECOVERY
STRETFORD TAIL GAS
63
64
OXIDIZER VENT GAS
STRETFORD SULFUR RECOVERY
DIESEL EMISSIONS
24
DUST EMISSIONS
PROCESSED SHALE MOISTENING WATER
70
71
ANHYDROUS AMMONIA
SOLID WASTE DISPOSAL
66
LIQUID SULFUR
65
SPENT LIQUOR TO RECLAIM
28
BOILER FEEDWATER
78
STRIPPED GAS LIQUOR
AERATED POND SLUDGE
RAW SHALE
1
22
RAW SHALE FINES
BAGHOUSE EMISSIONS
FUGITIVE DUST EMISSIONS
WASTE HEAT BOILER BLOWDOWN
77
REVEG WATER
91
103
111
DIESEL EMISSIONS
24
MINING & CRUSHING
92
RAW SHALE LEACHATE
WATER MANAGEMENT
SANITARY WATER TREATMENT SLUDGE
75
EXCESS MINE WATER
AERATION POND
DUST PALLIATIVES
90
4
TREATED WATER TO DISCHARGE
76
MINE WATER
SUBORE
2
OVERBURDEN
3

* Indicates streams that contact the environment.

BOXES WITH HEAVY LINES INDICATE POLLUTION CONTROL ACTIVITIES

Figure 3.1-2. Lurgi-Ruhrgas process operations and waste streams.
Source: EPA-600/8-8-83-005, 1983

to treatment by diethanolamine and triethylene glycol, which remove the acidic components and the residual moisture, respectively, from the compressed gas. The clean, dry gas is then sent to the pipeline. A small amount of spent amines are generated in this process, which are disposed with the processed shale. However, the spent amine is less than 1% of the processed shale mass.

The acid gas obtained from the diethanolamine regeneration is treated by the Stretford process, which converts the H_2S in the gas to elemental sulfur. The clean gas is then vented to the atmosphere. Spent Stretford liquor could be reclaimed on site or sent off site for reclamation.

The gas liquor from the oil and gas recovery section is subjected to oil/water separation, but it still contains dissolved ammonia and sulfur compounds and its direct discharge or use may also create pollution. Therefore, the ammonia and dissolved volatile compounds from the liquor are removed by an ammonia recovery process. The treated water is then used for processed shale moisturizing.

Overall water management activities consist of satisfying the process steam and cooling water needs, as well as efficient management of the aqueous waste effluents. Properly treated mine water is used as the boiler feedwater to produce the steam in the Lurgi waste heat recovery boiler. Treated mine water is also used as cooling water, process makeup water, cooling tower makeup water, etc. Minor wastes generated from the water treatments are equalized in a holding pond and then used for processed shale moisturizing.

Table 3.1-1 summarizes the final waste streams and the intermediate streams which make-up the final waste streams. These streams were identified in Figure 3.1-2. The subgrade ore, overburden, and processed shale (streams 2, 3, and 29) constitute the majority of the wastes (greater than 97% of solid wastes). Several wastewaters, such as equalization pond discharge, treated sanitary wastewater, clarified mine water, and oil/water separator discharge, are used to moisturize the processed shale.

Table 3.1-1 also describes the general composition of these streams and component mass flow rate. Of the final-waste streams, the processed shale represents more than 50% of the total volume. The components of concern and the composition of the solid waste streams show that for all the waste streams the leachable salts are of primary concern. The water for dust control and revegetation (streams 90 and 91) has a significant solids concentration which may contribute to salt leaching or metals leaching. Also of concern are the organics in the processed shale (generated from both the unburned hydrocarbons in the processed shale as well as from the moisturizing water (stream 78), and the sludges to be added to the solid waste pile.

Sanitary wastewater treatment and aerated pond sludges although not determined, can be estimated to be 0.5 lb/hr based on 18 gpm influent rate, a typical TSS concentration of 250 mg/L, and a treatment efficiency of 75%. Thus, at 0.5 lb/hr these sludges are of insignificant weight compared to the processed shale rates. However, the solids from sanitary wastewater treatment and sludges may pose special health risks and should not be dismissed lightly.

The rate of spent amine is difficult to estimate as the influent rate of rich amine and efficiency of the amine regenerator are uncertain.

3.1.3 Characteristics of Solid Wastes

Tables 3.1-2 to 3.1-6 provide additional information on the composition of the processed moisturized shale (stream 29). The nominal feed size of the particles associated with the Lurgi retorting process is less then 0.6 cm. As seen in Tables 3.1-2 and 3.1-3, properly moistened and compacted processed shale has low permeability; therefore, actual field leaching may not be represented by laboratory column leaching experiments. The results of column leaching and various other experiments performed on the processed shale are given in Tables 3.1-7 to 3.1-12. Some soluble elements are reported as their oxides.

TABLE 3.1-1. INVENTORY OF STREAMS TO BE DISPOSED OF AS SOLID WASTE IN THE LURGI-RUHRGAS PROCESS (63,000 BPSD Net Oil Production)

Stream number	Description of stream	Mass flow, 10^3 lb/hr (gpm)	Percent of total mass	Components of concern	Mass flow of component, lb/hr	Remarks[b]
Final Waste Streams[a]						
2	Subore	992	5.8	Particulates	520	The subore is crushed and disposed of with the processed shale. The dust from crushing is controlled with baghouses.
3	Overburden	5,175	30.5	Particulates	2,730	The overburden is crushed and disposed of with the processed shale. Dust from crushing is controlled with baghouses.
29	Moistened processed shale	9,733	57.4	Particulates Leachable salts	2,820 280,000	The processed shale is properly moisturized to reduce dust emissions. Proper compactions should reduce water permeability, hence leaching of salts.
59	Spent amine	N.D.[c]	<0.1	N.D.	N.D.	The amine spent during the reagent regeneration is removed periodically and sent for disposal.
90	Water for dust palliatives	753 (1,568)	4.4	TS	784	Clarified mine water is used for the raw and processed shale dust control.
91	Processed shale revegetation water	312 (649)	1.8	TS	325	Clarified mine water is used.
103	Sanitary water treatment sludge	N.D.	<0.1	N.D.	N.D.	The sludge from the sanitary water treatment is dewatered, then used as a fertilizer in revegetation.
111	Aerated pond sludge	N.D.	<0.1	N.D.	N.D.	The sludge may contain some bio-oxidized material and settled inorganic salts. It is sent for processed shale moisturizing.
Intermediate Streams						
-	Spent shale (not	(7,884)	-	--	--	Spent shale from process prior to moisturization.
28	Blowdown - waste heat boiler	21	-	TS	22	Clarified mine water is softened and demineralized before use in the boiler. The blowdown is used for processed shale moisturizing.
70	Stripped gas liquor	558 (279.7)	-	TSD NH_3 Dissolved organics	471 4 170	The free and fixed ammonia in the gas Liquor are recovered in the ammonia plant. Stripped liquor is used for processed shale moisturizing.

(continued)

TABLE 3.1-1 (continued)

Stream number[a]	Description of stream	Mass flow, 10^3 lb/hr (gpm)	Percent of total mass	Components of concern	Mass flow of component, lb/hr	Remarks[b]
Intermediate Streams (continued)						
78	Total processed shale moistening water	5,624	-	TDS	N.D.	Various wastewater streams are combined and used for for processed shale quenching and moisturizing.
	Humidified air cooler blowdown	661	-	TS	496	Treated mine water is used in the humidified air coolers in the oil recovery and Stretford processes. The blown down is used in processed shale moisturizing.
92	Raw shale leachate	N.D.	-	TDS DOC NH_3	3,490 mg/L 13 mg/L 5 µg/L	Leachate data are derived from a Tract C-a shale lysimeter study.
93	Storm runoff	150	-	N.D.	N.D.	Storm runoff water is collected and used for processed shale moisturizing.
	Mine water clarifier sludge	165	-	N.D.	N.D.	Suspended solids and debris are collected during the mine water clarification and used for processed shale moisturizing.
	Used sanitary water to municipal treatment	18	-	N.D.	N.D.	Used sanitary water is sent to municipal treatment before disposal.
	Treated sanitary water	18	-	--[d]	-	The sanitary water after municipal treatment is used for processed shale moisturizing.
	Boiler feedwater treatment concentrate	11	-	--	-	Regenerated waste from zoolite softening and demineralization is used for processed shale moisturizing.
	Cooling tower blowdown	1,123	-	TS	842	Treated mine water is used for plant cooling requirements. The quantity given does not include the humidified air cooler blowdown (Stream 88). The total blowdown would be 1,784 gpm.
	Equalization pond discharge to processed shale moistening to	2,525	-	N.D.	N.D.	Various wastewaters (e.g., sludges, concentrates, blowdowns) are combined and used for processed shale moisturizing.
	Clarified mine water to processed shale moistening	2,912	-	TDS	1,096	Clarified mine water is used to fulfill the processed shale moisturizing needs.

[a] Indicates streams that come into contact with the environment.

[b] The remarks indicate the stream disposition. The controls and treatments applied to the streams are those proposed for the Lurgi-Open Pit technologies.

[c] N.D. - not determined.

[d] Dashes (--) indicate no known components of concern.

Source: EPA-600/8-83-005, 1983

TABLE 3.1-2. PHYSICAL PROPERTIES OF LURGI PROCESSED SHALE

	Gradation							Compaction	
Test condition	Maximum particle size, in.	% Clay, 0.005 mm	% Silt, -200 mesh-0.005 mm	% Sand, 4-200 mesh	% Gravel, +4 mesh	Remarks	Specific gravity	Percent optimum moisture	Maximum density PCf
As received	3/8	17.1	47.8	33.4	1.7		2.83		
	3/8	15.3	46.4	36.6	1.7		2.84		
Compacted 1/2 D 698 (6,200 ft-lbs)	-	16.2	48.2	35.6	0.0	Initial		30.3	85.6
	-	17.6	44.2	38.2	0.0	After compaction			
	-	15.5	37.9	46.6	0.0	After triaxial shear test			
		15.5	37.9	46.6	0.0				
Compacted D 698 (12,375 ft-lbs)	-	16.2	48.2	35.6	0.0	Initial		28.5	88.2
	-	18.8	44.2	37.0	0.0	After compaction			
	-	8.8	42.5	48.7	0.0	After triaxial shear test			
Compacted D 1557 (56,250 ft-lbs)	-	16.2	48.2	35.6	0.0	Initial		23.2	96.8
	-	0.1	56.3	43.6	0.0	After compaction			
	-	12.8	45.9	41.3	0.0	After triaxial shear test			

	Permeability, ft/yr			Shear strength					
				Triaxial shear				Unconfined	
	Load, 50 psi	Load, 100 psi	Load, 200 psi	Friction coefficient, tan ø	Internal angle of friction, °	Cohesion, psi	Saturated cohesion, psi	Days cured @ 120°F	Unconfined compression, psi
As received									
Compacted 1/2 D 698 (6,200 ft-lbs)	0.002	0.003	-	0.69	34.5	22.2	7.6	0	28.8
								0	33.1
								7	590.7
								7	785.9
								14	575.0
								14	682.4
								28	-
								28	-
Compacted D 698 (12,375 ft-lbs)	0.003	0.005	-	0.62	32.0	33.3	13.9	0	38.5
								0	42.5
								7	874.5
								7	865.5
								14	940.8
								14	912.1
								28	1,222.2
								28	1,222.1
Compacted D 1557 (56,250 ft-lbs)	0.001	0.001	-	0.80	38.5	41.0	27.8	0	378.5
								0	350.8
								7	971.1
								7	1,182.6
								14	986.5
								14	1,081.0
								28	-
								28	-

Source: EPA-600/8-83-005, 1983

TABLE 3.1-3. SUMMARY OF HYDRAULIC CONDUCTIVITY MEASUREMENTS FOR VARIOUS COMPACTION AND LOADINGS FOR LURGI RETORTED SHALE

Material	Water wt. %	Density, g/cm^3	Permeability, cm/s at various loadings 50 psi	100 psi	200 psi
LURGI-RG-I[b]	26.6	1.41	1.0×10^{-6}	6.5×10^{-7}	6.5×10^{-7}
	10.4	1.33	3.0×10^{-5}	1.9×10^{-5}	2.0×10^{-5}
LURGI-ULG-I[a,b]	dry	1.81	8.3×10^{-5}	-	-
LURGI-RB[a,b]	dry	1.22	1.2×10^{-5}	-	-

[a] Leaching columns.

[b] Various source samples.

Source: EPA-600/D-84-228, 1984

TABLE 3.1-4. WATER HOLDING CAPACITY[a] OF LURGI PROCESSED SHALES AT VARIOUS PRESSURES AND BULK DENSITIES

Sample	Pressure 14.7 psi (1 bar)	44.1 psi (3 bar)	73.5 psi (5 bar)	147 psi (10 bar)	200 psi (13.6 bar)
No compaction					
Lurgi	27.5	27.6	26.9	25.3	15.5
Packed to a BD[b]=1.30 g/cc					
Lurgi ash	62.4	62.3	62.2	62.0	61.7
BD[b]=1.45 g/cc					
Lurgi ash	60.2	58.7	56.6	55.5	55.2
BD[b]=1.60 g/cc					
Lurgi ash	47.2	46.3	45.8	44.4	43.7
Lurgi	20.7	20.2	19.8	19.8	19.0

[a] Table entries are moisture contents (w) expressed on a weight % basis: weight of water per unit weight of dry solids.

[b] BD= bulk density.

Source: EPA-600/D-84-228, 1984

TABLE 3.1-5. COMPOSITION OF LURGI PROCESSED MOISTURIZED SHALE

Component	Weight percent	Mass flow, 10^3 lb/hr	Flow, 10^3 lb-moles/hr
Retorted shale (moisturized)	100.00	9,733	-
Moisture	18.70	1,820	101.1
Oxygen (organic)	0.02	2	0.1
Nitrogen (organic)	0.08	8	0.6
Carbon (organic)	0.25	24	2.0
Sulfur (total)	0.93	91	2.8

Source: EPA-600/8-83-005, 1983

TABLE 3.1-6. INORGANIC ANALYSIS OF LURGI THE PROCESSED SHALE

Component	Weight percent
Silicon dioxide	46.00
Iron oxides	4.40
Aluminum oxide	12.70
Calcium oxide	22.40
Magnesium oxide	4.80
Sulfate	3.80
Sodium oxide	3.20
Potassium oxide	2.70
Carbonate	4.40
Chloride	0.08
Loss on ignition	4.60

Source: EPA-600/8-83-005, 1983

TABLE 3.1-7. MAJOR ION COMPOSITION OF COLUMN LEACHATE-LURGI RETORTED SHALE

$\frac{vt}{L}$	mg/L								
	Ca	Mg	Na	K	Cl	HCO_3	CO_3	SO_4	pH
0.020	575	0.3	11970	950	1360	136	393	23900	10.83
0.058	560	0.2	11270	760	1300	67	351	23400	11.09
0.092	540	0.4	10590	830	1150	57	328	21900	11.13
0.186	520	0.6	5410	300	450	29	208	12600	11.22
0.236	530	0.7	3150	220	230	25	149	5590	11.15
0.292	540	0.7	1660	160	131	26	123	5450	11.05
0.350	560	0.8	1000	120	75	26	101	3890	10.96
0.378	570	0.7	795	110	65	22	111	3480	11.07
0.452	580	0.7	600	110	45	21	105	3180	11.08
0.535	600	0.7	575	100	48	21	118	3110	11.12
0.590	590	0.6	535	110	39	20	90	3040	11.02
0.652	590	0.7	405	100	30	18	93	2760	11.07
0.737	600	0.7	530	110	41	23	105	3180	11.02
0.860	610	0.7	385	80	26	20	136	2770	11.21
1.06	590	0.8	365	120	23	20	137	2750	11.20

Key

Average permeability = $\bar{K}$ = 8.3 x 10^{-5} cm/s

$\frac{vt}{L}$ = pore volume

Source: EPA-600/D-84-228, 1984

TABLE 3.1-8. CONCENTRATION OF SELECTED TRACE ELEMENTS IN COLUMN LEACHATE OF LURGI RETORTED SHALE

$\frac{vt}{L}$	mg/L						
	F	B	Si	Mo	Mn	Al	Sr
0.020	21.0	1.01	20	11	0.037	29	7.8
0.058	22.7	0.77	11	11	0.023	23	7.9
0.092	17.5	0.66	15	10	0.022	18	16
0.186	8.2	0.41	11	5.1	0.018	5.8	6.9
0.236	4.4	0.33	11	3.7	0.017	4.6	8.4
0.292	8.6	0.24	11	2.4	0.019	3.8	13
0.350	7.9	0.16	8	1.9	0.015	3.3	13
0.378	10.1	0.14	8	1.9	0.013	3.2	15
0.452	6.1	0.10	8	1.6	0.013	2.9	16
0.535	6.3	0.10	8	1.6	0.010	2.8	17
0.590	4.5	0.16	5	1.0	0.016	1.5	19
0.652	5.4	0.12	9	1.5	0.024	2.7	19
0.737	4.1	0.10	9	1.7	0.019	2.9	19
0.860	4.8	0.09	9	1.3	0.012	2.5	17
1.06	4.4	0.22	8	1.2	0.015	2.3	22

Key

Average permeability = $\bar{K} = 8.3 \times 10^{-5}$ cm/s

$\frac{vt}{L}$ = pore volume

Source: EPA-600/D-84-228, 1984

TABLE 3.1-9. CONCENTRATIONS IN ASTM WATER SHAKE TEST EXTRACTS - LURGI SPENT SHALES

Parameter	Units	RG-I[a]	ULG-I[a]	RB[a]
pH	-	11.43	11.49	11.85
EC	μmhos/cm @ 25°	3660	2650	4270
ALK	mg/L	192	160	355
H_2CO_3	mg/L	0.001	0.001	0.001
HCO_3	mg/L	9.6	7.0	6.9
CO_3	mg/L	110.7	92.5	209.6
TDS	mg/L	3700	2140	3350
F	mg/L	2.0	3.8	6.34
Cl	mg/L	23.7	10.9	17.1
PO_4	mg/L	0.62	<0.1	0.5
NO_3	mg/L	8.7	1.7	2.52
SO_4	mg/L	2545	1301	2291
Zn	mg/L	0.001	0.007	<0.001
Fe	mg/L	0.018	<0.005	<0.005
Co	mg/L	<0.005	<0.005	<0.005
Li	mg/L	0.371	0.616	0.887
V	mg/L	0.053	0.059	0.082
NH_3	mg/L	8.4	6.2	-
B	mg/L	0.173	0.005	0.096
Cd	mg/L	<0.001	<0.001	<0.001
Be	mg/L	<0.0005	<0.0005	<0.0037
Mg	mg/L	0.6	0.5	0.4
P	mg/L	0.22	0.20	0.5
Si	mg/L	5.5	3.4	5.4
Mo	mg/L	<0.05	<0.05	<0.05
Mn	mg/L	0.008	0.006	0.029
Ni	mg/L	<0.005	<0.005	<0.005
Na	mg/L	324	180	275
Cu	mg/L	<0.001	0.003	0.002
Al	mg/L	0.60	<0.02	<0.02
Ca	mg/L	750	402	713
Ba	mg/L	0.115	0.130	0.157
K	mg/L	43	34	64
Cr	mg/L	0.100	<0.005	0.095
Sr	mg/L	14	13	20
Pb	mg/L	0.012	<0.01	<0.01
Ag	mg/L	<0.001	0.005	0.008
Ti	mg/L	<0.005	<0.005	<0.005
Se	mg/L	<0.020	<0.020	<0.020
As	mg/L	0.016	<0.01	<0.01
Hg	mg/L	<0.001	0.001	<0.001

[a] Various source samples.
Source: EPA-600/D-84-228, 1984

TABLE 3.1-10. CONCENTRATIONS IN RCRA TEST EXTRACTS - LURGI SPENT SHALES

Parameter	Units	RG-I[a]	ULG-I[a]	RB[a]
pH	-	8.06	7.99	8.67
EC	µmhos/cm @ 25°	4150	4230	5650
ALK	mg/L	1612	2188	2505
H_2CO_3	mg/L	37.8	59.7	14.1
HCO_3	mg/L	1948	2646	2937
CO_3	mg/L	9.5	11.1	58.7
TDS	mg/L	5690	6520	8520
Cl	mg/L	7.1	6.4	18.9
PO_4	mg/L	<0.01	<0.01	<0.01
NO_3	mg/L	1.53	0.48	0.53
SO_4	mg/L	684	420	880
Zn	mg/L	0.138	0.082	0.010
Fe	mg/L	<0.005	<0.005	<0.005
Co	mg/L	<0.005	<0.005	<0.005
Li	mg/L	0.173	0.135	0.304
V	mg/L	0.008	0.006	0.008
NH_3	mg/L	3.28	1.08	1.98
B	mg/L	0.520	0.270	1.470
Cd	mg/L	0.004	0.003	0.002
Be	mg/L	<0.0005	0.0016	0.0026
Mg	mg/L	290	269	430
P	mg/L	0.4	0.7	0.7
Si	mg/L	0.6	7.0	7.9
Mo	mg/L	<0.05	<0.05	<0.05
Mn	mg/L	0.110	0.410	0.090
Ni	mg/L	0.012	0.075	<0.005
Na	mg/L	43	28	55
Cu	mg/L	0.032	0.017	0.009
Al	mg/L	<0.02	<0.02	<0.02
Ca	mg/L	964	1280	1479
Ba	mg/L	0.130	0.350	0.180
K	mg/L	3.2	5.0	11.0
Cr	mg/L	<0.005	<0.005	<0.005
Sr	mg/L	8.9	13	13
Pb	mg/L	<0.01	<0.01	<0.01
Ag	mg/L	0.002	<0.002	<0.002
Ti	mg/L	<0.005	<0.005	<0.005
Se	mg/L	<0.02	0.020	<0.02
As	mg/L	0.019	0.020	0.047
Hg	mg/L	<0.001	0.001	<0.001

[a] Various source samples.
Source: EPA-600/D-84-228, 1984

TABLE 3.1-11. LEACHABLE MASS AS INDICATED BY THE ASTM PROPOSED WATER SHAKE TEST FOR LURGI SPENT SHALES - mg/g

Parameter	RG-I[a]	ULG-I[a]	RB[a]
Na	1.296	0.720	-
Ca	3.00	1.608	-
Mg	0.002	0.002	0.0008
SO_4	10.18	5.204	-
Cl	0.095	0.044	-
F	0.008	0.015	-
B	0.0007	-	0.0002
Mo	0.004	0.002	0.010
Al	0.002	0.006	0.008
TDS	14.80	8.560	-

[a] Various source samples.
Source: EPA-600/D-84-228, 1984

TABLE 3.1-12. LEACHABLE MASS AS INDICATED BY THE RCRA EXTRACTION TEST FOR LURGI SPENT SHALES - mg/g

Parameter	RG-I[a]	ULG-I[a]	RB[a]
Na	0.860	0.560	1.100
Ca	19.28	25.60	29.58
Mg	5.80	5.38	8.60
SO_4	13.68	8.40	1.760
Cl	0.142	0.128	0.378
B	0.010	0.005	0.029
Mo	0.016	0.008	0.020
Al	0.050	0.038	0.038
TDS	113.8	130.4	170.4

[a] Various source samples.
Source: EPA-600/D-84-228, 1984

3.2 TOSCO II OIL SHALE RETORTING

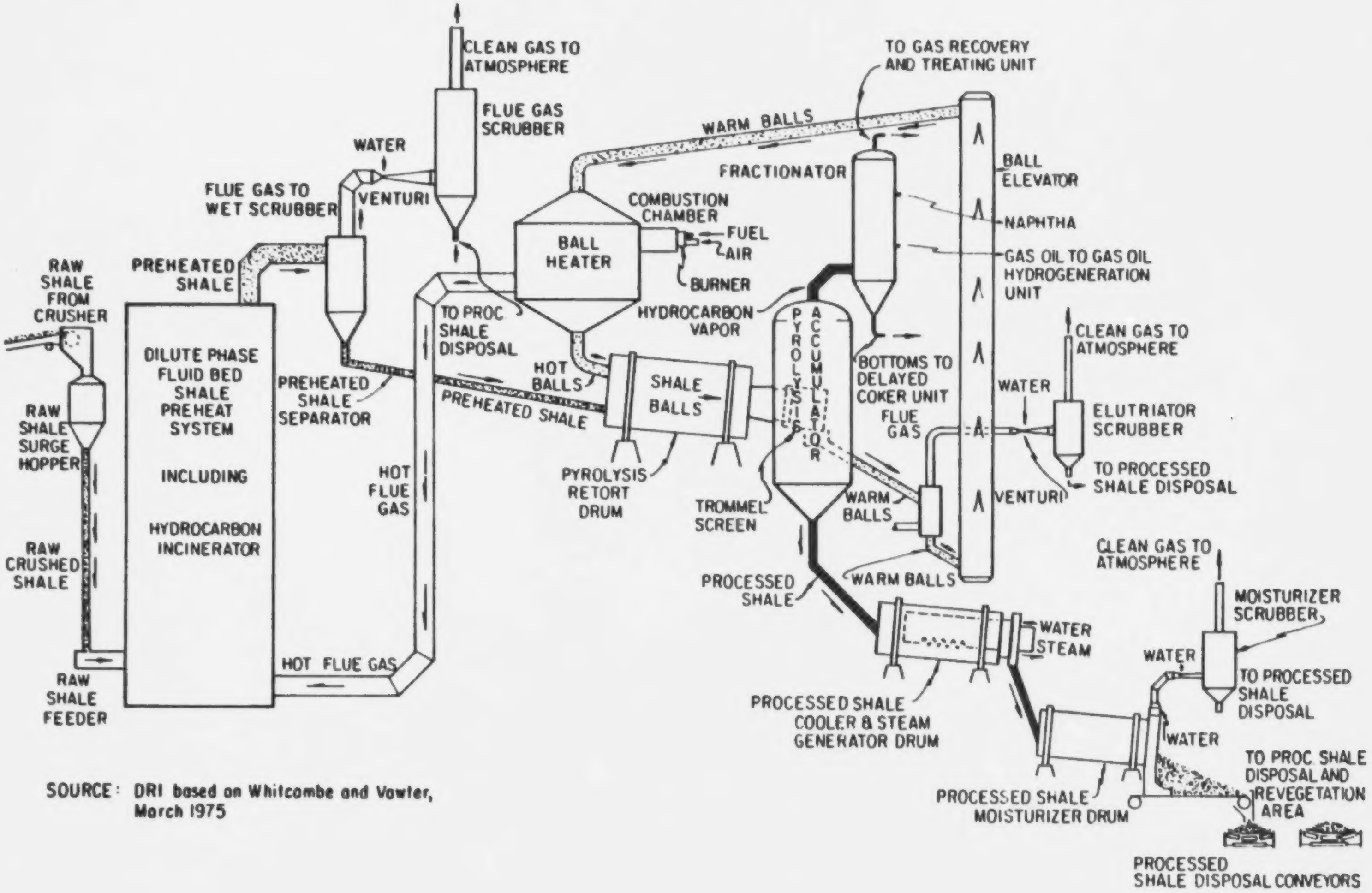
3.2.1 Retorting Operation

Figure 3.2-1 shows a conceptual flow diagram of the TOSCO II retorting process [EPA-600/8-83-003, April 1983]. The process is indirectly heated and employs a solid-to-solid heat exchange (between hot ceramic balls and raw shale) as a means for providing the heat of retorting. The integral parts of the TOSCO II retorting system are: retort and accumulator; product fractionator; processed shale removal system; ceramic ball system; and raw shale preheat system.

The TOSCO II retort is a slightly inclined, rotating drum to which raw shale, minus 1/2-inch size, preheated to approximately 500°F, is fed. Ceramic balls, at 1.5 times the shale mass flow rate, and previously heated to about 1,300°F, are also added to the retort. The rotating, mixing action results in pulverization of the raw shale. Heat transfer from the ceramic balls raises the shale temperature to approximately 900°F, and pyrolysis, or retorting, of the kerogen in the shale occurs. The pyrolysis vapors and the mixture of balls and pyrolyzed shale are then taken to an accumulator vessel. This accumulator consists of a rotating, perforated screen or trommel which retains the balls but allows the pulverized shale to pass through, thus affording a separation of the two. The pyrolysis vapors are removed from the vapor dome at the top of the accumulator and sent to a fractionator for oil recovery, while the ceramic balls are sent for recycling and the processed shale is eventually sent for disposal.

In the oil recovery section (not shown in Figure 3.2-1), the pyrolysis vapors are separated by the fractionator into gas, naphtha oil, gas oil, bottom oil, and gas condensate, or foul water. Each stream is sent to its respective processing unit for appropriate treatment.

Processed shale dust, contained with the ceramic balls as they emerge from the accumulator, is removed by hot flue gas from the steam superheater. The particulate matter is subsequently converted to a sludge in the venturi wet scrubber and sent to the disposal area. The clean flue gas is emitted to the atmosphere through the scrubber stack. The clean ceramic balls are then transported by a bucket elevator to the ball heater for heating and recycling back to the retort. In the ball heater, treated fuel gas and shale oil are burned by atomizing the fuels with air in a vertical combustion chamber at the top of the vessel. Hot flue gas thus generated passes downward, concurrently with the balls, thereby heating them. The flue gas is separated from the balls in the gas disengagers and the hot balls are returned to the retort.


CLEAN GAS TO ATMOSPHERE
FLUE GAS SCRUBBER
WATER
FLUE GAS TO WET SCRUBBER
VENTURI
TO GAS RECOVERY AND TREATING UNIT
WARM BALLS
FRACTIONATOR
BALL ELEVATOR
COMBUSTION CHAMBER
FUEL
AIR
BALL HEATER
BURNER
NAPHTHA
GAS OIL TO GAS OIL HYDROGENERATION UNIT
RAW SHALE FROM CRUSHER
PREHEATED SHALE
HYDROCARBON VAPOR
TO PROC SHALE DISPOSAL
DILUTE PHASE FLUID BED SHALE PREHEAT SYSTEM
INCLUDING
HYDROCARBON INCINERATOR
PYROLYSIS
ACCUMULATOR
CLEAN GAS TO ATMOSPHERE
BOTTOMS TO DELAYED COKER UNIT
HOT BALLS
SHALE BALLS
RAW SHALE SURGE HOPPER
PREHEATED SHALE SEPARATOR
PREHEATED SHALE
WATER
ELUTRIATOR SCRUBBER
FLUE GAS
HOT FLUE GAS
PYROLYSIS RETORT DRUM
TROMMEL SCREEN
WARM BALLS
VENTURI
TO PROCESSED SHALE DISPOSAL
RAW CRUSHED SHALE
CLEAN GAS TO ATMOSPHERE
PROCESSED SHALE
WARM BALLS
MOISTURIZER SCRUBBER
WATER
STEAM
WATER
HOT FLUE GAS
TO PROCESSED SHALE DISPOSAL
RAW SHALE FEEDER
PROCESSED SHALE COOLER & STEAM GENERATOR DRUM
WATER
TO PROC SHALE DISPOSAL AND REVEGETATION AREA
PROCESSED SHALE MOISTURIZER DRUM
PROCESSED SHALE DISPOSAL CONVEYORS

SOURCE: DRI based on Whitcombe and Vawter, March 1975

Figure 3.2-1. TOSCO II OIL SHALE RETORTING PROCESS

Source: EPA-600/8-83-003, April 1983

The hot processed shale from the accumulator is taken to a rotating drum steam generator/cooler where it is cooled to about 300°F by indirect heat transfer to the feedwater to generate some process steam. The cooled processed shale is then taken to another rotating drum and processed shale moisturizing water is added. Steam incidentally produced during the moisturizing operation entrains some processed shale dust which is removed in the venturi wet scrubber; the steam, along with a little particulate matter, is released to the atmosphere through the scrubber stack. The processed shale, cooled to below 200°F is moisturized to approximately 14% water by weight (to aid compaction and dust control) and then transported to the disposal area.

The disengaged hot flue gas is used to preheat the raw shale feed, thereby recovering most of the waste heat. The preheating system consists of a series of three lift pipes (or preheat zones), a thermal oxidizer (incinerator), cyclones and wet scrubbers. The flue gas is introduced at the bottom of the last lift pipe (first preheat zone), where the raw shale stream from the second lift pipe (second preheat zone) is also received. The solids are lifted pneumatically and heat transfer from the gas to the shale occurs. The preheated shale is accumulated in a collecting bin at the top of the lift pipe and sent to the retort. Residual dust in the flue gas is separated by a cyclone and added to the feed going to the retort.

Since the flue gas temperature is at its highest when introduced to the last lift pipe (first preheat zone), it partially retorts the very fine shale, which results in hydrocarbon vapor release into the flue gas. Therefore, the flue gas is introduced to a thermal oxidizer (located between the first and second preheat zones) to burn the hydrocarbons so that the hydrocarbon emission to the atmosphere is not excessive. Some shale oil, C_4 liquids, and air are also added to the oxidizer to sustain combustion. The resulting flue gas is cooled, and then introduced to the bottom of the other two lift pipes. At this point, the temperature of the flue gas is low enough so that the extent of retorting of the fine shale is less than in the first preheat zone. Hydrocarbons released in these two lift pipes are emitted with the flue gas, without incineration.

The flow diagram for a complete plant complex, emphasizing the waste streams produced, is presented in Figure 3.2-2 [TOSCO, 1982]. Production-scale mining of the oil shale is accomplished by conventional underground room-and-pillar mining.

The acid gases (H_2S, CO_2) in the retort gas and hydrotreated flue gas are separated by absorption in a diethanolamine solution as a pretreatment step. The treated sweet gas is eventually separated into C_4 liquids, LPG, and C_2 and lighter process gas. Sulfur from the acid gases is recovered by the Claus/Wellman-Lord processes.

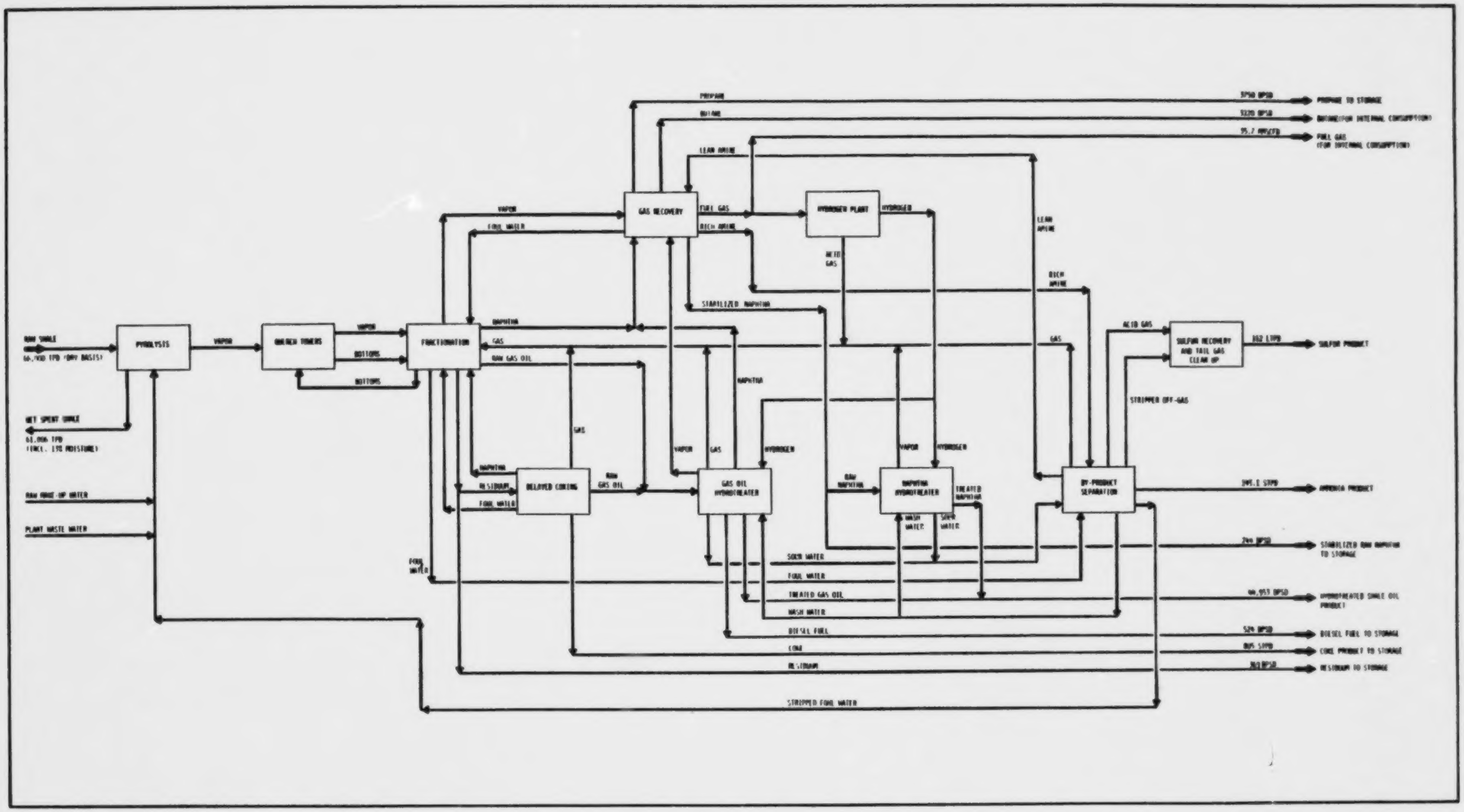

RAW SHALE
66,930 TPD (DRY BASIS)
WET SPENT SHALE
61,066 TPD
(INCL. 13% MOISTURE)
RAW MAKE-UP WATER
PLANT WASTE WATER
PYROLYSIS
VAPOR
QUENCH TOWERS
VAPOR
BOTTOMS
BOTTOMS
FRACTIONATION
NAPHTHA
GAS
RAW GAS OIL
VAPOR
FOUL WATER
GAS RECOVERY
PROPANE
BUTANE
LEAN AMINE
FUEL GAS
RICH AMINE
STABILIZED NAPHTHA
HYDROGEN PLANT
HYDROGEN
ACID GAS
LEAN AMINE
RICH AMINE
GAS
ACID GAS
SULFUR RECOVERY AND TAIL GAS CLEAN UP
STRIPPER OFF-GAS
162 LTPD
SULFUR PRODUCT
3750 BPSD
PROPANE TO STORAGE
3320 BPSD
BUTANE (FOR INTERNAL CONSUMPTION)
35.7 MMSCFD
FUEL GAS
(FOR INTERNAL CONSUMPTION)
GAS
NAPHTHA
RESIDUUM
FOUL WATER
DELAYED COKING
RAW GAS OIL
VAPOR
GAS
NAPHTHA
HYDROGEN
GAS OIL HYDROTREATER
RAW NAPHTHA
VAPOR
HYDROGEN
NAPHTHA HYDROTREATER
TREATED NAPHTHA
WASH WATER
SOUR WATER
BY-PRODUCT SEPARATION
395.1 STPD
AMMONIA PRODUCT
FOUL WATER
SOUR WATER
FOUL WATER
TREATED GAS OIL
WASH WATER
DIESEL FUEL
COKE
RESIDUUM
STRIPPED FOUL WATER
244 BPSD
STABILIZED RAW NAPHTHA TO STORAGE
44,953 BPSD
HYDROTREATED SHALE OIL PRODUCT
524 BPSD
DIESEL FUEL TO STORAGE
805 STPD
COKE PRODUCT TO STORAGE
363 BPSD
RESIDUUM TO STORAGE

Figure 3.2-2. Process block flow diagram for sand wash processing facility.
Source: TOSCO, 1982

A tail gas stream containing a small amount of sulfur dioxide is eventually emitted from the Wellman-Lord unit. An acidic condensate is also obtained from the Wellman-Lord unit; it is neutralized with alkali and then sent for disposal.

The naphtha and gas oils are hydrotreated to produce upgraded syncrude. An ammoniacal wash water is produced from the hydrogenation and subjected to an ammonia recovery process. This latter process produces a sulfurous overhead which is sent to the Claus Plant for recovery of sulfur. The hydrotreatment operations consume process gas, thereby generating flue gases. The ammonia plant does not burn any fuels. The bottoms oil is coked to yield a gaseous overhead, naphtha oil, and gas oil which are sent to their respective units for treatment, and a coke residue which is disposed of with the processed shale or marketed. A small amount of aqueous condensate is also produced and sent to the foul water stripper. A gas-fired furnace is used for heating the feed to the coke drums. The flue gas from the furnace is emitted to the atmosphere. Hydrogen for the oil hydrotreating is generated by steam reforming, using the treated process gas (C_2 and lighter fraction). The reforming furnaces burn fuel and generate a flue emission. Carbon dioxide, generated as a result of reforming, is separated from the hydrogen and is also released to the atmosphere.

The foul water condensed from the pyrolysis vapors is steam stripped to remove volatile matter which is sent to the Claus plant for recovery of sulfur. Ammonia in the stripper overheads is converted to elemental nitrogen during incineration in the Claus process. The stripped water is used in processed shale moisturizing.

3.2.2 Solid Wastes

Large quantities of solid waste materials will be generated over the life of a TOSCO Plant. Solid wastes are summarized in Tables 3.2-1 [TOSCO, May 1982] and 3.2-2 [EPA-600/8-83-003, April 1983].

3.2.3 Characteristics of Solid Wastes

Various data on TOSCO II processed shales are presented in Tables 3.2-3 to 3.2-9. Table 3.2-10 presents the composition of TOSCO II combined process wastewater (retort water and other wastewaters). Tables 3.2-11 to 3.2-13 depicts chemical composition data on the TOSCO II foul water. Lab leachate data on retorted shale are shown in Tables 3.2-14 to 3.2-16. Tables 3.2-17 and 3.2-18 depict field leachate data for the TOSCO II retorted shale.

TABLE 3.2-1. SUMMARY OF SOLID WASTES ESTIMATED FOR THE TOSCO SAND WASH PROCESSING FACILITY

Waste material	Source	Estimated quantity, ton/yr	Estimated volume, cubic yards/yr
	Sanitary landfill		
Sanitary refuse	Surface mine and plant site	3,000	8,500
Construction debris	Surface mine and plant site	2,500	7,000
TOTAL		5,500	15,500
	Potential hazardous wastes		
Spent catalysts			
Spent HDN catalyst	Upgrading units	305	500
Guard bed catalyst (proprietary solids)	Upgrading units	570	900
Spent HDS catalyst	Hydrogen unit (hydrodesulfurizer)	18.3	35.9
Spent ZnS catalyst	Hydrogen unit (ZnO guard bed reactor)	6.7	17.9
Spent FE-CR catalyst	Hydrogen unit (high temp shift converter)	14.2	25.4
Spent Cu-Zn catalyst	Hydrogen unit (low temp shift converter)	33.7	54.4
Spent reforming catalyst	Hydrogen unit (reformers)	12.8	19.8
Spent methanation catalyst	Hydrogen unit (methanation)	5.4	8.4
Spent alumina catalyst	Sulfur unit	80	100
Spent sludge (DEA filtration)	Gas recovery	14.25	12.6
TOTAL		1,070.4	1,674.4
Others			
Separator sludge	API separator	500	720
Tank bottom sludge	Water treatment area	2,000	2,400
Plant debris	Mine and plant site	50	200
TOTAL		2,550	3,320

NOTE: This table does not list sediment produced by treatment of the raw water since the sediment may be suitable for reclamation and will be combined with the spent shale in the spent shale moisturization procedure.

Source: TOSCO, May 1982

TABLE 3.2-2. MAJOR WASTE PRODUCED OVER A PERIOD OF 20 YEARS FOR TOSCO II 47,000 bbl/day PLANT WITH UPGRADING

Stream description	Quantity, 10^6 tons	Material quantity as a percent of total waste quantity
Raw shale runoff and leachate	N.D.[a]	N.D.
Raw shale sludge - preheat system	11.31	2.27
Processed shale sludge - Ball elutriator	0.85	0.17
Processed shale sludge - moisturizer	0.57	0.11
Processed shale	350.84	70.43
Stripped foul water	18.49	3.71
Compression condensate - Wellman-Lord unit	1.73	0.35
Coke[b]	5.26	1.06
Stripped sour water purge stream	0.75	0.15
Revegetation water	14.59	2.93
Dust suppression water	9.70	1.95
Boiler blowdown	11.04	2.22
Boiler feedwater treatment concentrate	4.81	0.97
Cooling tower blowdown	60.31	12.11
Storm runoff	4.34	0.87
Processed shale leachate	N.D.	N.D.
Spent catalysts	0.005	0.001
Treated sanitary water	0.55	0.11
Sanitary water treatment sludge	N.D.	N.D.
Service and fire water runoff	0.63	0.13
Source water clarifier sludge	2.37	0.48
Trash, construction debris, etc.	N.D.	N.D.
TOTAL	498.15	99.93

[a] N.D. - not determined.

[b] May be a marketable by-product.

Source: EPA-600/8-83-003, April 1983

TABLE 3.2-3. PHYSICAL PROPERTIES OF TOSCO II PROCESSED SHALE

Parameter	Unit	Quantity
Geometric mean size	cm	0.007
Geometric standard deviation	-	3.27
Permeability	cm^2	2.5×10^{-10}
Bulk density	g/cc	1.30
Solids density	g/cc	2.59
Porosity	-	0.47
Maximum size	cm	<0.476
Minimum size	cm	>0.00077

Source: EPA-600/8-83-003, 1983

TABLE 3.2-4. SIEVE ANALYSIS OF TOSCO II SPENT OIL SHALE RESIDUE

Sieve U.S. standard	Opening, mm	Weight retained in grams	Percent retained	Cumulative percent finer
No. 8	2.38	0	0.00	100.00
No. 16	1.19	567	5.14	94.86
No. 30	0.595	390	3.53	91.33
No. 50	0.297	588	15.33	86.00
No. 120	0.125	1,170	10.60	75.40
No. 200	0.074	784	7.10	68.30
Hydrometer	0.0461	1,134	10.28	58.02
	0.0346	1,125	10.20	47.82
	0.0336	2,043	18.50	29.32
	0.0268	2,882	26.10	3.22
	0.0157	287	2.60	0.62
	0.0077	69	0.62	0.00
Summation		11,038	100.00	

Source: Margheim, May 1975

TABLE 3.2-5. HYDRAULIC CONDUCTIVITY MEASUREMENTS OF TOSCO II RETORTED SHALE

Material	Moisture, wt. %	Density, g/cm³	Permeability at various loadings 50 psi	100 psi	200 psi
TOSCO II	20.8	1.56	6.8×10^{-6}	6.2×10^{-6}	5.6×10^{-6}
	11.0	1.39	5.6×10^{-5}	4.6×10^{-5}	3.9×10^{-5}
	11.4	1.29	6.7×10^{-5}	4.0×10^{-5}	2.5×10^{-5}
TOSCO II[a]	Dry	1.46	2.8×10^{-5}		

[a] Leaching columns.

Source: EPA-600/D-84-228, 1984

TABLE 3.2-6. WATER HOLDING CAPACITY[a] OF TOSCO II PROCESSED SHALES AT VARIOUS PRESSURES AND BULK DENSITIES

Sample	Pressure 14.7 psi (1 bar)	44.1 psi (3 bar)	73.5 psi (5 bar)	147 psi (10 bar)	200 psi (13.6 bar)
No compaction	48.0	45.8	45.9	43.8	44.7
Packed to a BD[b]=1.30 g/cc	42.2	42.0	41.9	41.6	41.4
BD[b]=1.45 g/cc	36.0	33.8	32.9	32.1	30.5
BD[b]=1.60 g/cc	34.6	33.5	32.1	30.8	30.5

[a] Table entries are moisture contents (w) expressed on a weight % basis: weight of water per unit weight of dry solids.

[b] BD = bulk density.

Source: EPA-600/D-84-228, 1984

TABLE 3.2-7. REPORTED ANALYSIS OF TOSCO II PROCESSED SHALE[a]

Component	Weight percent
Hydrogen (organic)	0.44
Oxygen (organic)	NR[b]
Nitrogen (organic)	0.35
Carbon (organic)	4.49
Sulfur (total)	0.76
Na_2O	8.68
K_2O	3.28
CaO	15.80
MgO	5.31
Al_2O_3	6.80
SiO_2	33.00
Fe_2O_3	2.52
CO_2	20.92
Loss on ignition at 900°C	27.60

[a] Dry basis.

[b] NR - not reported.

Source: EPA-600/D-84-228, 1984

TABLE 3.2-8. SELECTED ELEMENTAL CONCENTRATIONS IN RAW AND RETORTED TOSCO II OIL SHALES

	Weight, %			PPM	
	Raw shale	Retorted shale		Raw shale	Retorted shale
Org C	-	5.5	F	1,020	1,490
C	-	-	Sr	640	780
H	-	-	Ba	1,310	1,580
N	-	-	Mn	271	334
S	-	-	B	110	146
Ca	9.8	11.3	As	70	82
K	1.25	1.50	Cu	48	62
Mg	2.6	3.9	Cr	36	42
Na	1.43	1.74	Pb	30	41
Si	13.0	16.0	Ni	29	34
Al	3.4	4.2	Zn	72	105
Fe	1.89	2.45	Mo	28	36
			Se	4.1	4.9
			Cd	1.05	0.98

Source: Wildung and Zachara, 1980.

TABLE 3.2-9. SOME POLYCYCLIC AROMATIC HYDROCARBONS THAT HAVE BEEN DETECTED IN THE BENZENE EXTRACT OF TOSCO II SPENT SHALES

Compound	ppb (W/W)
Benzo(a)pyrene (BaP)	28-55
Alkyl I (BaP)	-
Alkyl II (BaP)	-
Benzo(ghi)fluoranthene	-
Benzo(e)pyrene	18-29
Perylene	3-9
Benzo(ghi)perylene	12-24
Anthanthrene	3-5
Pyrene	58-102
Fluoranthene	21-23
Benz(a)anthracene	27-45
Triphenylene	13-34
Penanthrene	
7,12-Dimethylbenz(a)anthracene	-
3-Methylcholanthrene	-
Coronene	5
Chrysene	30-35

Source: Fox, July 1983

TABLE 3.2-10. APPROXIMATE COMPOSITION OF TOSCO II COMBINED PROCESS WASTEWATER (50,000 bbl/day upgraded shale oil production)

Component	Concentration in water (mg/L) added to spent shale	Kg/hr
Ca^{+2}	280	86
Mg^{+2}	100	32
Na^{+1}	670	204
$NH_4{}^{+1}$	16	4.5
Zn^{+2}	5	1.8
As^{+5}	0.015-0.3	0.0045-0.09
Cr^{+6}	2	0.45
$CO_3{}^{-2}$	360	109
$HCO_3{}^{-1}$	100	32
$SO_4{}^{-2}$	850	261
$S_2O_3{}^{-2}$	90	27
$PO_4{}^{-3}$	5	1.8
Cl	570	175
CN^{-1}	5	1.81
Phenols	315	98
Amines	410	127
Organic acids	1,330	409
Neutral oils	960	295
TOTALS (rounded)	6,100	1,870

NOTE: In addition to above, elements present in trace quantities (less than 1 mg/L) are Pb, Ce, Ag, Mo, Zr, Sr, Rb, Br, Se, Cu, Ni, Co, Fe, Mn, V, Ti, K, P, Al, F, B, Li.

Source: DRI No. 5269, April 1980

TABLE 3.2-11. ORGANIC CONTENT OF GAS CONDENSATE (FOUL WATER) FOR TOSCO II

Component	Concentration, mg/L	Mass % of organics
Acids	1,710	39
Phenols	510	12
Bases	680	16
Neutrals	1,424	33
TOTAL	4,324	100
TOC	3,160	73

Source: EPA-600/8-83-003, April 1983

TABLE 3.2-12. COMPOSITION OF FOUL WATER FOR TOSCO II

Component	Amount in raw shale[a] lb/ton	Foul water flow lb/hr (gpm)	Coker wash water flow[b] lb/hr (gpm)	Total foul water lb/hr (gpm)	Total foul water mg/L
NH_3	0.28	770	-	770	3,088
H_2S	0.036	99	386	485	1,945
CO_2	0.34	935	-	935	3,749
Organic acids	0.155	426	-	426	1,710
Organic phenols	0.046	127	-	127	510
Organic bases	0.062	170	-	170	680
Organic neutrals	0.129	355	-	355	1,424
H_2O	-	213,300 (426)	36,050 (72)	249,350 (498)	-
TOTAL		216,182	36,436	252,618	

[a] Pilot plant data obtained from Metcalf & Eddy Engineers, October 1975.

[b] Estimated from material balances based on data from Colony Development Operation, 1974, and Whitcombe and Vawter, March 1975.

Source EPA-600/8-83-003, April 1983

TABLE 3.2-13. INORGANIC SPECIES IN TOSCO II FOUL WATER

Component	Concentration, mg/L
Ca^{++}	6
Mg^{++}	2
Na^{+}	5
K^{+}	0.4
HCO_3^{-}	-
$CO_3^{=}$	-
Cl^{-}	5
F^{-}	0.3
$S_2O_3^{=}$	-
CN^{-}	12
Si	1.3
Other components	**Range, mg/L**
Fe	1-10
B	0.1-1.0
Ce, Ag, Sr, Rb, Br, Se, As, Zn, Cu, Ni, Mn, Ti, P, Al	0.01-0.1
Pb, Ba, Mo, Zr, Co, Cr, Li	0.001-0.01

Source: EPA-600/8-83-003, April 1983

TABLE 3.2-14. CONCENTRATIONS IN ASTM WATER SHAKE AND RCRA EXTRACTS - TOSCO II SPENT SHALES

		ASTM		
Parameter	Units	4:1	20:1	RCRA
pH	-	8.69	9.01	7.72
EC	μmhos/cm @ 25°	2650	740	5710
ALK	mg/L	164	96	2737
H_2CO_3	mg/L	0.88	0.24	140
HCO_3	mg/L	191	107	3325
CO_3	mg/L	4.0	4.7	7.5
TDS	mg/L	1970	510	8180
F	mg/L	20.2	7.5	-
Cl	mg/L	9.8	1.9	22.2
PO_4	mg/L	<0.03	<0.03	<0.01
NO_3	mg/L	16.0	19.5	2.0
SO_4	mg/L	1130	238	229
Zn	mg/L	0.020	<0.005	0.078
Fe	mg/L	0.018	<0.005	<0.005
Co	mg/L	<0.005	<0.005	<0.005
Li	mg/L	0.079	0.039	0.084
V	mg/L	0.007	<0.002	0.006
NH_3	mg/L	0.644	0.067	0.60
B	mg/L	2.500	0.530	0.640
Cd	mg/L	<0.001	<0.001	0.003
Be	mg/L	<0.0005	<0.0005	0.0045
Mg	mg/L	35	14	81
P	mg/L	0.18	<0.05	0.6
Si	mg/L	0.8	0.28	1.2
Mo	mg/L	1.56	0.35	<0.05
Mn	mg/L	0.053	0.004	1.260
Ni	mg/L	<0.005	0.070	0.055
Na	mg/L	545	116	131
Cu	mg/L	<0.001	0.018	0.014
Al	mg/L	2.15	3.75	<0.02
Ca	mg/L	31	17	1872
Ba	mg/L	0.117	0.084	0.780
K	mg/L	8	1.7	3.9
Cr	mg/L	0.025	0.018	0.007
Sr	mg/L	0.53	0.35	16
Pb	mg/L	<0.010	<0.010	<0.01
Ag	mg/L	<0.001	<0.001	0.002
TL	mg/L	0.006	<0.005	<0.005
Se	mg/L	<0.020	<0.020	<0.02
As	mg/L	0.018	0.010	<0.01
Hg	mg/L	<0.001	0.001	0.075

Source: EPA-600/D-84-228, 1984

TABLE 3.2-15. LEACHABLE MASS AS INDICATED BY RCRA AND ASTM WATER SHAKE SHAKE EXTRACTION TEST FOR TOSCO II SPENT SHALES - mg/g

Parameter	RCRA	ASTM
Na	2.620	2.18
Ca	37.44	0.124
Mg	1.620	0.140
SO_4	4.580	4.52
Cl	0.444	0.039
F	-	0.081
B	0.013	0.010
Mo	0.010	0.006
Al	0.054	0.009
TDS	163.6	7.88

Source: EPA-600/D-84-228, 1984

TABLE 3.2-16. EFFLUENT CONCENTRATIONS - (TOSCO II) SPENT SHALES. CONSTANT RATE INJECTION INTO A DRY COLUMN

$\frac{vt}{L}$	Ca	Na	Cl mg/L	SO_4	F	pH
0.020	545	10,095	178	25,000	27.0	9.24
0.050	540	10,060	172	25,200	29.0	9.28
0.100	520	10,540	176	27,400	30.0	9.29
0.121	505	10,570	167	26,700	30.2	9.39
0.264	495	10,520	154	26,800	39.2	9.37
0.287	425	9,815	163	26,800	36.3	9.31
0.308	410	9,355	152	25,500	34.0	9.34
0.333	455	9,440	139	24,100	23.2	9.28
0.355	435	8,590	133	23,400	28.4	9.30
0.375	395	7,965	114	21,500	15.9	9.27
0.397	415	7,420	100	20,500	17.2	9.29
0.418	380	6,705	92	17,000	37.8	9.26
0.440	345	5,770	84	15,900	32.6	9.21
0.464	352	5,490	74	14,400	33.3	9.17
0.488	320	4,885	61	13,500	17.7	9.25
0.511	330	4,185	54	12,100	17.7	9.21
0.534	300	3,744	49	11,200	18.2	9.20
0.556	275	3,425	45	10,300	19.7	9.13
0.579	265	3,075	32	9,400	18.3	9.20
0.629	252	2,605	29	7,920	19.1	9.20
0.965	120	1,280	19	3,210	29.2	9.10
1.030	83	945	13	2,470	29.5	9.21
1.120	90	1,060	16	2,820	29.1	9.24
1.191	72	715	12	1,820	30.5	9.27
1.886	26	485	7	1,010	33.5	9.35
2.013	14	375	6	660	38.5	9.38
2.25	13	420	7	840	31.1	9.25

Key

$K = 2.8 \times 10^{-5}$ cm/s

$\frac{vt}{L}$ = pore volume

Source: EPA-600/D-84-228, 1984

TABLE 3.2-17. LEVELS OF TRACE ELEMENTS MEASURED IN RUNOFF AND LEACHATES FROM FIELD TEST PLOTS OF TOSCO II RETORTED SHALE (ppm)

Element	Runoff from typical rain storms	First leachate from sloping section of plot	First leachate from deepest portion of bed
Be	-	0.0006	-
Hg	0.00002-0.00007	0.0005	0.0003
Cd	-	0.006	0.003
Sb	-	0.001-0.003	0.002
Se	0.004-0.007	0.002-2	2
Mo	0.03-0.09	3-74	5-74
Co	0.01	0.01	0.001-0.04
Ni	0.05	0.05-0.02	0.2-0.6
Pb	0.009	0.004	0.003
As	0.005-0.008	0.02	0.08-0.2
Cr	0.01-0.07	0.004-0.009	0.004
Cu	0.02	0.06-0.2	0.06-0.2
Zr	0.001	0.001	0.003
B	-	0.02-0.9	0.02
Zn	0.01-0.09	1	1-3
Li	0.02-0.2	0.007-0.076	0.07-0.8
V	0.003	0.003-0.006	0.004-0.1
Mn	0.004	0.06-0.2	0.06-0.5
F	0.02-3	2-17	0.006-12
Ba	0.02-0.04	0.06-0.1	0.1
Fe	0.09-0.6	0.6-2	1-3

Source: EPA-600/8-83-003, 1983

TABLE 3.2-18. INORGANIC COMPOSITION OF TOSCO II LEACHATES PRODUCED DURING LABORATORY AND FIELD LYSIMETER STUDIES (mg/L)

	Laboratory studies			
	Batch (Runnells and Eammaili, 1981)	Batch (Runnells and Eammaili, 1981)	Column first pore volume (Stollenwerk, 1980)[a]	Blender (Margheim, 1975)
Al	7.6	20	≤0.1	-
As	<0.2	0.6	≤0.02	-
B	5.2	11.5	10	-
Ba	<0.02	0.017	-	-
Br	<1	<1	1.3	-
Ca	1.6	1.0	470	114
Cd	<0.02	<0.02	-	-
Cl	22	52	230	7.6
Co	<0.02	<0.02	-	-
Cr	<0.01	<0.01	0.12	-
Cu	0.03	<0.01	0.08	-
DOC	96	-	73	-
EC (µmhos/cm)	-	-	-	1750
F	76	155	26	-
Fe	<0.01	≤0.02	0.24	-
HCO_3	-	-	390	20
Hg	≤0.05	≤0.06	-	-
K	8	10.6	77	32
Li	≤0.1	0.2	-	-
Mg	0.4	<0.3	1700	27
Mn	0.01	0.01	0.42	-
Mo	3.2	6.3	3.9	-
Na	815	1865	4700	165
Ni	<0.02	<0.02	<0.04	-
NH_4	2	≤2	7.7	-
NO_2	3	3	<0.2	5.6
NO_3	<0.5	<0.5	<0.1	-
Oil and grease	-	-	-	-
Pb	<0.1	<0.1	<0.03	-
PO_4	<1	3	0.18	-
Rb	-	-	0.18	-
S	530	1300	-	-
Sediment	-	-	-	-
Se	<0.3	<0.3	0.02	-
Si	0.12	1.4	6.5	-
SO_4	625	1700	15,700	730
Sn	<0.15	<0.18	<0.06	-
Sr	0.07	0.05	9.8	-
TDS	2185	5480	-	1262
TOC	-	-	-	-
U	<0.5	<0.5	-	-
V	0.12	0.61	-	-
Zn	<0.01	<0.01	≤0.03	-
pH (units)	9.9	10.3	8.0	8.4
Bulk density, g/cm^3	-	-	1.15	-
Solid-to-liquid ratio	0.4 g/mL	1.0 g/mL	2.8 g/mL	0.1 g/mL
Contact time	17 days	17 days	46 days	5 min.
No. of replicates	2	4	4	1

(continued)

TABLE 3.2-18 (continued)

	Field lysimeter studies			
	Runoff (Margheim, 1975)	Snowmelt runoff (Ward and Reinecke, 1972)	Rainfall runoff (Metcalf and Eddy, 1975	Percolation (Metcalf and Eddy, 1975)
Al	-	-	0.06-0.2^{b}	0.09-2
As	-	-	0.005-0.008^{b}	0.02-0.2
B	-	-	-	0.02-0.9
Ba	-	-	0.02-0.04^{b}	0.01-0.1
Br	-	-	0.02	0.1-0.7
Ca	10-232	9-83	15-140	420-550
Cd	-	-	-	0.003-0.006
Cl	-	-	-	-
Co	-	-	0.01^{b}	0.001-0.07
Cr	-	-	0.01^{b}	0.003-0.009
Cu	-	-	0.02	0.06-0.2
DOC	-	-	-	-
EC (µmhos/cm)	88-1415	58-572	300-1800	-
F	-	-	1.5-24	5.2-18
Fe	-	-	0.1-0.3^{b}	<1-8
HCO_3	20-25	13-89	-	-
Hg	-	-	0.00002-0.00007^{b}	$<3x10^{-6}$-$5x10^{-4}$
K	-	<0.1-1.8	4.3-33	59-140
Li	-	-	0.02^{b}	0.007-0.8
Mg	<0.06-16	0.9-22	13-23	64-315
Mn	-	-	0.004^{b}	0.06-0.5
Mo	-	-	0.03^{b}	3-76
Na	<1-74	0.2-11	35-518	7820-17,825
Ni	-	-	0.02-0.05^{b}	0.05-0.6
NH_4	-	-	-	-
NO_3	-	-	-	-
NO_2	-	-	-	-
Oil and grease	-	-	7-18	50-163
Pb	-	-	-	0.003-0.004
PO_4	-	-	-	-
Rb	-	-	0.004-0.03^{b}	0.01-0.03
S	-	-	-	-
Sediment	1300-5500	-	1790-27,450	14-120
Se	-	-	0.004-0.007^{b}	0.4-2
Si	-	-	0.3-1^{b}	4-8
SO_4	7-726	16-239	-	29,110-31,120
Sn	-	-	-	0.003-0.005
Sr	-	-	0.2^{b}	4-6
TDS	-	-	243-4518	28,425-57,137
TOC	-	-	2-10	284-647
U	-	-	-	-
V	-	-	0.01^{b}	0.003-0.01
Zn	-	-	0.01-0.09^{b}	0.9-3
pH (units)	7.74-8.52	7.58-8.95	7.4-8.15	2.5-4.8
Bulk density, g/cm^3	1.39	1.39	1.36	1.36
Solid-to-liquid ratio	0.46-1.0	<0.01-0.08	0.79	0.79
Contact time	3.6 hours	1.4, 4.2 hrs.	20 min-48 hrs	-
No. of replicates				

[a] Samples collected and analyzed in quarter pore volumes. Recorded value is average for four samples collected over first completed pore volume.

[b] Average or # range for two samples of runoff collected 16 and 48 hrs. after start of rainfall. Analyses by spark source mass spectrometry, except H_g which is by flameless atomic absorption spectrometry.

Source: Fox, July 1983

3.3 PARAHO DIRECT HEATING MODE OIL SHALE RETORTING

3.3.1 Retorting Operation

The Paraho retort was developed by modifying the USBM vertical kiln technology [Shih, 1979]]. In demonstration runs at Anvil Points, Colorado, the Paraho direct mode was used to produce more than 100,0000 barrels of shale oil for the U.S. Navy. It was refined to products meeting all specifications.

A schematic diagram of the Paraho direct mode is presented in Figure 3.3-1. The crushed shale, flowing downward, is contacted with a countercurrent stream of hot gases having sufficient heat content to pryolyze the kerogen in the shale. The oil is carried out of the top of the retort as a stable mist with the gas stream, and the retorted shale is removed from the bottom of the retort through a hydraulically-operated grate. The process is continuous.

Raw oil shale, crushed to a 1/4 to 3 in. size, is spread evenly across the top of the shale bed in the retort where it is preheated by the rising hot gases. Raw shale fines, less than 1/4 in. are screened from the retort feed to avoid lowering the bed porosity and increasing the resistance to the countercurrent gas flow. The shale moves downward by gravity through the mist formation and preheating zone into the retorting zone where the temperature is increased to retorting temperatures to produce gas, oil, and coke. This residue of coke, or char, about 4.5 per cent by weight of organic carbon, remains on the shale. As the shale continues downward into the combustion zone, much of the heat used for direct mode retorting is supplied by the combustion of the coke residue. Air, used for combustion, is mixed with recycle gas to control flame temperatures and assure even gas distribution. This air-gas mixture is introduced at several levels in the combustion zone. Additional recycle gas is introduced through the bottom grate to cool the shale as it passes through the cooling zone. The retorted shale leaves the retort at approximatley 300°F. The hot gases are cooled by the incoming shale in the mist formation zone to approximately 145°F to produce a stable oil mist. The oil mist is separated from the offgas by oil mist separators (coalescers) and an electrostatic precipitator. The oil yield from the Paraho direct mode is about 93 percent of Fischer assay. Part of the oil-free gas is recycled to the retort and the remainder is available as plant fuel.

3.3.2 Solid Waste

The process operations for the Paraho direct mode process are presented in Figure 3.3-2. This figure shows the block-flow diagram for commercial-scale operations designed for the Paraho-Ute project in Utah [Paraho, June 1982]. Raw shale mining, crushing, screening, and stockpiling will generate dusts that will be controlled by a variety of control devices. The raw shale dust,

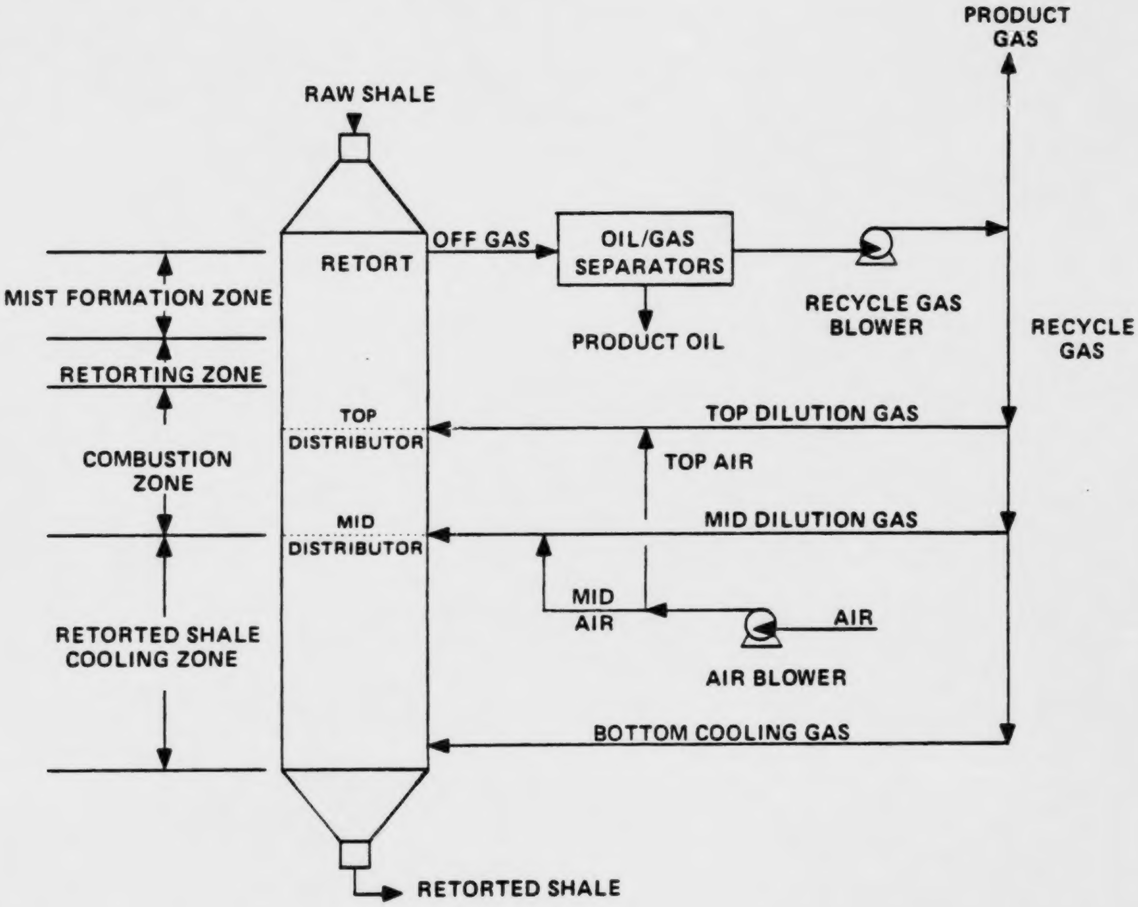

PRODUCT GAS
RAW SHALE
OFF GAS
OIL/GAS SEPARATORS
RETORT
MIST FORMATION ZONE
RECYCLE GAS BLOWER
RECYCLE GAS
PRODUCT OIL
RETORTING ZONE
TOP DISTRIBUTOR
TOP DILUTION GAS
COMBUSTION ZONE
TOP AIR
MID DISTRIBUTOR
MID DILUTION GAS
MID AIR
AIR
RETORTED SHALE COOLING ZONE
AIR BLOWER
BOTTOM COOLING GAS
RETORTED SHALE

Figure 3.3-1. Schematic of Paraho direct heating mode process.
Source: DOE/EV-0086, June 1980

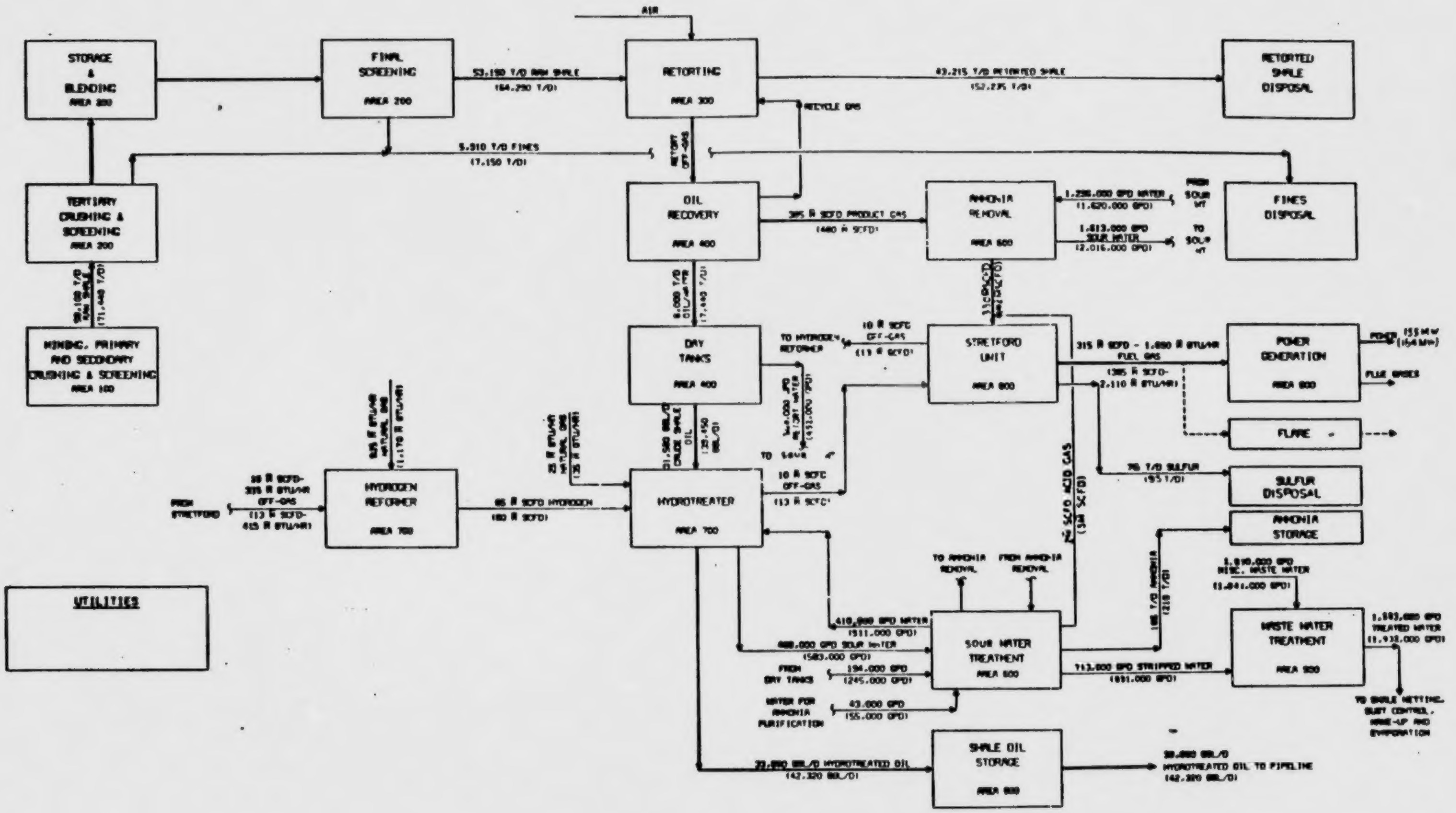

AIR
STORAGE & BLENDING AREA 200
FINAL SCREENING AREA 200
53,190 T/D RAW SHALE (64,290 T/D)
RETORTING AREA 300
43,215 T/D RETORTED SHALE (52,235 T/D)
RETORTED SHALE DISPOSAL
RECYCLE GAS
5,910 T/D FINES (7,150 T/D)
RETORT OFF-GAS
TERTIARY CRUSHING & SCREENING AREA 200
59,100 T/D RAW SHALE (71,440 T/D)
MINING, PRIMARY AND SECONDARY CRUSHING & SCREENING AREA 100
OIL RECOVERY AREA 400
385 M SCFD PRODUCT GAS (480 M SCFD)
AMMONIA REMOVAL AREA 600
1,296,000 GPD WATER (1,620,000 GPD)
FROM SOUR WT
1,613,000 GPD SOUR WATER (2,016,000 GPD)
TO SOUR WT
FINES DISPOSAL
8,000 T/D OIL/WATER (17,440 T/D)
DRY TANKS AREA 400
TO HYDROGEN REFORMER
10 M SCFG OFF-GAS (13 M SCFD)
STRETFORD UNIT AREA 800
315 M SCFD - 1,690 M BTU/HR FUEL GAS (385 M SCFD- 2,110 M BTU/HR)
POWER GENERATION AREA 800
POWER 155 MW (164 MW)
FLUE GASES
FLARE
76 T/D SULFUR (95 T/D)
SULFUR DISPOSAL
AMMONIA STORAGE
SCFD ACID GAS (SM SCFD)
346,000 GPD WATER (431,000 GPD)
TO SOUR WT
31,580 BBL/D CRUDE SHALE OIL (39,450 BBL/D)
FROM STRETFORD
10 M SCFD- 335 M BTU/HR OFF-GAS (13 M SCFD- 415 M BTU/HR)
HYDROGEN REFORMER AREA 700
825 M BTU/HR NATURAL GAS (1,170 M BTU/HR)
85 M SCFD HYDROGEN (80 M SCFD)
25 M BTU/HR NATURAL GAS (35 M BTU/HR)
HYDROTREATER AREA 700
10 M SCFC OFF-GAS (13 M SCFC)
UTILITIES
TO AMMONIA REMOVAL
FROM AMMONIA REMOVAL
410,000 GPD WATER (511,000 GPD)
468,000 GPD SOUR WATER (583,000 GPD)
FROM DRY TANKS
194,000 GPD (245,000 GPD)
WATER FOR AMMONIA PURIFICATION
43,000 GPD (55,000 GPD)
SOUR WATER TREATMENT AREA 600
185 T/D AMMONIA (218 T/D)
713,000 GPD STRIPPED WATER (891,000 GPD)
1,890,000 GPD MISC. WASTE WATER (1,041,000 GPD)
WASTE WATER TREATMENT AREA 900
1,593,000 GPD TREATED WATER (1,932,000 GPD)
TO SHALE WETTING, DUST CONTROL, MAKE-UP AND EVAPORATION
33,880 BBL/D HYDROTREATED OIL (42,320 BBL/D)
SHALE OIL STORAGE AREA 800
33,880 BBL/D HYDROTREATED OIL TO PIPELINE (42,320 BBL/D)

Figure 3.3-2. Paraho Commercial Process Flowsheet
Source: Paraho, June 1982

collected by these devices will be disposed as a solid in the raw shale fines storage area. Future plans call for the utilization of these raw shale fines for their energy value. The total raw shale rejects (fines plus dust) will be about 7,500 tons per day.

The Paraho direct mode retorting operation, designed to produce 42,300 barrels of hydrotreated shale oil per day, will produce about 52,000 tons of retorted shale per day. This represents, by far, the largest solid waste stream. The retorted shale will be disposed in an above-ground site designed to minimize water infiltration, runoff, and percolation. The retorted shale will be transferred from the retort to the disposal area using covered conveyors, an enclosed silo, and covered bottom dump trucks. The bulk of the shale will be spread in 8 to 10 in. layers, wetted to about 10% by weight on the surface for dust control, and subjected to light compaction.

Additional water will be used to construct special water-imperious liners and, in case of emergencies, to control excessive temperatures. This water, used for retorted shale dust control, liner construction, and emergency temperature control, will consist of a mixture of treated process water and river water. Water usage for both raw shale fines storage and retorted shale disposal will be about 925 gal. per minute.

The crude shale oil, obtained from the oil recovery system, is dewatered and subjected to on-site hydrotreating to produce a pipeline quality, marketable product. This hydrotreating and its auxiliary processes produce a variety of spent catalysts which constitute potential solid wastes.

The product gas, hydrotreater offgas, and wastewater offgas are subjected to ammonia and sulfur recovery prior to being used as plant fuel. Sulfur recovery, will produce additional solid wastes.

Sour water from oil recovery, hydrotreating, ammonia plant and Stretford units is treated in a wastewater treater. This treatment will produce additional solid wastes.

Finally, solid wastes will be generated from normal construction, scrap, and sanitary wastes.

The amounts of these solid waste streams and their characteristics have been compiled in Table 3.3-1. Although these wastes are presented as average annual rates, most of these materials are not processed on a daily basis. Detailed characterization data are not available.

Only a portion of these solids wastes will be disposed onsite. The oily particulates and many of the spent catalysts will be used as feedstocks on offsite reclamation plants. The hazardous wastes will be transported to an approved offsite hazardous waste disposal area.

The dusts (raw shale, retorted shale, surficial soils, overburden, and unit operations) produced from the Paraho-Ute facility will be about 250 tons per day [Paraho, 1982].

3.3.3 Characteristics of Solid Wastes

The retorted shale produced by the Paraho direct mode operations has been subjected to extensive characterization studies. These retorted shale physical and chemical characteristics are compiled Tables 3.3-2 to 3.3-4. Detailed physical properties are available in the literature. Due to the varied research operations performed during most of these characterization studies, along with variations of these studies, these data exhibit wide variations and inevitable uncertainty.

Since all of the water produced during the retorting and auxiliary operations will be treated and used for dust control (co-disposed with the retorted shale), the characteristics of these process waters are listed in Tables 3.3-4 to 3.3-9. At the present time, there have been two types of process water that have been studied: the product water (Tables 3.3-4 to 3.3-8), co-produced with the crude shale oil and separated from oil tank bottoms; gas condensate, (Table 3.3-9) water condensed from the product gas after oil-water separation. The data in Table 3.3-9 contain uncertainties about the operation and may not depict actual commercial operations.

Tables 3.3-10 and 3.3-11 present leachate data from the RCRA and ASTM water shake tests. Table 3.3-12 presents data from laboratory tests in which certain pore volumes of water were passed through a column of shale. Finally Table 3.3-13 summarizes field data obtained from field lysimeter studies.

It should be noted that various investigators have studied characteristics of solid wastes for Paraho Direct process. Only selected data are presented in the above mentioned Tables 3.3-2 to 3.3-13.

TABLE 3.3-1. PARAHO DIRECT SOLID WASTES: TYPES AND QUANTITIES (42,300 barrel per day plant)

Solids waste	Quantity & design case rates	Thousand tons/year[a]
Construction debris and garbage	16,000 cu yd (first 3 years)	5.3[b]
Raw shale fines	7,385 TPSD (max)	2,450[c]
Retorted shale	52,235 TPSD	17,250
Wastewater treatment sludge	2,468 TPSD (wet basis, 0.6% solids)	4.8
Sulfur, crystalline cake	95 TPSD	31.4
Scrap and garbage	4.6 T/D	1.6
Oil filter particles	64 TPSD (50% oil)	21.1[d]
ZnO catalyst	250 cu ft/6 mo	18.8[d]
Lo-temp CO shift catalyst	2,600 cu ft/2 yr	488[d]
Methanator catalyst	600 cu ft/2 yr	11.5[d]
Reformer catalyst	1,500 cu ft/2 yr	25[d]
Hydrotreater catalyst (ICR-106)	(Confidential)	
API separator bottoms	0.9 T/D	0.3[e]
Air floatation unit float	0.09 T/D	0.03[e]
High-temp CO shift catalyst	1,750 cu ft/2 yr	32.8[e]
Arsenic guard bed catalyst	9,600 cu ft/6 mo	720[e]

[a] Estimated solids

[b] Construction only.

[c] Not a waste; feeds taken for future use.

[d] Not a waste; feeds taken for reclamation.

[e] Off-site disposal, EPA-approved site.

Source: Paraho , June 1982 and Heistand, 1984.

TABLE 3.3-2. PARAHO DIRECT RETORTED SHALE CHARACTERISTICS

A. Size Classification

Unified Soil Classification System

Designation	Size, mm	Weight percent
Cobble	+38.1	3.9
Gravel	4.76 - 38.1	51.8
Sand	0.074 - 4.76	21.7
Silt	0.005 - 0.074	20.7
Clay	-0.005	1.9

B. Density

Compactive effort ft.-lb/cu. ft.	Water Added Density, lb/cu. ft. None	Water Added Density, lb/cu. ft. Optimum, 22 wt. %
Light, 6,200	86	88
Std. Proctor, 12,375	90	93
Heavy, 56,250	96	98

C. Strength

Days curing	Compressive strength, psi
28	190
60	200

D. Permeability

Compactive effort ft.-lb/cu. ft.	Loading psi	Permeability, ft/yr No water	Permeability, ft/yr Optimum water
Light, 6,200	50	40	6.3
	100	27	1.3
	200	18	0.8
Heavy, 56,250	50	35	1.0
	100	30	0.6
	200	23	0.1

Source: Holtz, 1976.

TABLE 3.3-3. PARAHO DIRECT RETORTED SHALE
MAJOR ELEMENTS (wt. %)

Elements	WCC	BNW1	CSM	BNW2	Battelle	Paraho	DRI
Aluminum	1.27	4.7		4.6	4.83		
Calcium	11.5	13.4	12.0	13.4	13.3		
Carbon, min.	4.95				3.73	4.42	
Carbon, org.	1.86				2.39	2.31	
Iron	2.03	2.45	2.31	2.56	2.40		
Magnesium	4.22	4.21	4.47		4.32		
Nitrogen					0.58	0.22	0.3
Potassium	0.6	1.82	1.85		1.86		
Silicon	16.1	17.7		18.0	13.2		
Sodium	1.48	2.24		2.36	2.19		
Sulfur					0.48	0.77	0.8
Titanium		0.22		0.22			

NOTES AND SOURCES:
WCC [Holtz, 1976]
BNW1 - weighted means, August 1977 [DOE/EV-0086, June 1980]
CSM - means, August-September 1977 [DOE/EV-0086, June 1980]
BNW2 - weighted means, November 1977 [DOE/EV-0086, June 1980]
Battelle [Battelle PNL 3830]
Paraho - means, 1977-1978 [DOE/EV-0086, June 1980]
DRI [DRI, June 1977]

TABLE 3.3-4. PARAHO DIRECT RETORTED SHALE TRACE ELEMENTS (ppm)

Elements	A	B	C	D	E	F	G
Antimony	2.8		2.9		0.7		
Arsenic	59	60	44	21	59	30	54
Barium	625	586	737		800		
Beryllium	-	-	-	2	-	-	-
Boron	120	190	96	52	107	65	100
Bromine	0.8		<1		0.6		
Cadmium	0.9			0.6			
Cerium	52						
Cesium	4.7						
Chromium	41		37	136	44		
Cobalt	10		11	13			
Copper	53	42	57	44	56		
Dysprosium	2.4						
Europium	0.71		0.82				
Fluorine		1900	1000	1660	1000	150	
Gallium	11.5	7.8	11.7				
Hafnium	2.1		2.1				
Holmium	0.9						
Lanthanum	24						
Lead	34	32	33	18	35		
Lutecium	0.4						

(continued)

TABLE 3.3-4 (continued)

Elements	A	B	C	D	E	F	G
Manganese	416	332	411	600	396		
Mercury	0.03		0.02	0.07	0.04	0.06	
Molybdenum	33	43	33	12	31	16	28
Nickel	34	35	35	38	32		
Niobium	10.3	7.0	7.0				
Rubidium	85	97	87				
Samarium	4.1		3.6				
Scandium	7.1		7.0				
Selenium	2.9	1.6	3.3	0.3	3.3	0.5	2.0
Strontium	832	935	877		800		
Tantalum	0.7						
Terbium	0.4						
Thorium	7.0	7.5					
Uranium	5.2						
Ytterbium	16	14	15				
Zinc	85	68	71	16	82		
Zirconium	70	68	71	42			

NOTES AND SOURCES:

A - BNW, weighted means, August 1977 [DOE/EV-0086, June 1980]
B - CSM, means, August-September 1977 [DOE/EV-0086, June 1980]
C - BNW, weighted means, November 1977 [DOE/EV-0086, June 1980]
D - TRW, May 1977
E - Battelle PNL 3830
F - DRI, June 1977
G - Stollenwork and Rumell, 1981

TABLE 3.3-5. PARAHO DIRECT PRODUCT WATER[a]
BULK PROPERTIES (wt. %)

Date	Lab	C	N	S	Min CO_2	Alkalinity	pH
5/77	PAR	5.1	3.7	3.5	3.0		
6/77	PAR	4.3	2.9	4.3	3.4		
7/77	PAR	4.1	3.1	5.1	2.1		
8/77	BNW	2.4	2.2	3.9 - 5.1			
8/77	PAR	3.0	2.1	3.5	2.7		
9/77	PAR	4.5	3.0	2.7	4.1		
9/77	CSM				3.1		8.8 - 8.9
10/77	PAR	4.6	2.9	3.8	4.3		
11/77	BNW			2.2 - 4.8			8.5 - 8.6
11/77	PAR	4.3	2.8	4.4	4.5		
12/77	PAR	2.4	2.6	4.5	3.9		
1/78	PAR	3.6	2.4	4.4	4.4		8.5
2/78	PAR	5.4	3.0	3.9	3.5		
4/78	PAR	4.0	1.7	3.1	0.8		
5/78	PAR	7.4	3.8	5.7	4.7		
6/78	CSM			2.8 - 3.1		2.6 - 7.8	8.6 - 9.1
6/78	PAR	5.9	6.1	4.3	2.2		
7/78	CSM			2.7 - 2.9	2.5	2.9 - 3.7	8.5 - 8.9
7/78	PAR	4.8	3.9	4.3	3.2		
8/78	PAR	6.1	4.4	4.4	3.0		
8/78	BNW						8.6
9/78	PAR	8.1	5.6	6.5	1.0		

Other species:
H_2S, <10 ppm; SO_4, 0.02-1.08 wt. %; NH_3, 1.4-3.6 wt. %;
TOC, 1.4-4.4 wt. %; Cl, 1.3-2.8 wt. %

---

[a] Product water - water CO-produced with oil in the gas-oil separator.

Source: DOE/EV-0086, June 1980.

TABLE 3.3-6. PARAHO DIRECT PRODUCT WATER MAJOR SPECIES/GROSS SALINITY (ppm)

Date	Source	Al	Cl	Ca	Fe	Mg	K	Na	$SO_4^=$	Si	Total dissolved solids	Comments
8-24-77	DNW	<100		<100	<100	<100	<100	<100		<100		INAA
		<0.4	36	38.4	3	460	38	106/115				INAA
					1.5		17	111		44		AA
										37		PES
8-25-77	BNW	0.26	65	2000	1.8	220	<20	104/103				INAA
				35.9		258	8	112		25		AA
										22		PES
					2.6							XRF
8/26/77	BNW	0.7		64	4.2	960	65	39.6				INAA
										23		PES
										24		AA
1-04-78	PAR	<1		23.8	4.5	400	3.2	215		48		AA
									15,000		119.4	Precip.
6-01-78	PAR	<1		0.30	8.4	680	18.6	340		16		AA
			81									Titr.
									3,300		148.1	Precip.

(continued)

TABLE 3.3-6 (continued)

Date	Source	Al	Cl	Ca	Fe	Mg	K	Na	$SO_4^=$	Si	Total dissolved solids	Comments
11-15-77	BNW	<1		43	1.9	870	<30	335				INAA
										34		PES
										35		AA
11-16-77	BNW	<2	71	42	1.9	790	<30	316				INAA
										20		PES
										28		AA
11-17-77	BNW	0.4	1.6	41	<7	320	<10	73				INAA
										36		PES
					5.4			70		41		AA
					2.1							XRF
9-78	CE-TEMPO			30.3	3.0	1190	67.5	521				AA
									8,500			Turbidimetric
12-13-78	CSRI	0.8	1	18	28	16	17	4		12		

Source: DOE/EV-0086, June 1980

TABLE 3.3-7. PARAHO DIRECT PRODUCT WATER TRACE ELEMENTS (ppm)

	6/77 PAR[a]	8/77 BNW[a]	9/77 GE-T[a]	11/77 BNW[a]	12/77 GSRI[a]	1/78 PAR[a]	Jackson[b]	DRI[c] and Jackson[b]
Sb								1
As	9.0	3.1-6.9	22.2	4.9-18.2	6	9	1.5-9.0	0.01 (5.1)
Ba	<0.5	0.8	0.4	<3	0.3	<0.5	0.1	
B	30	43	13	16-43	0.2	40	0.1-3.6	3
Cd	0.3				<0.2	0.1	0.1	0.5
CN	8.8						1.6	
Cr							0.14	(0.1)
Cu	0.2	0.5-0.9	2.6	0.5-11.8		2.5		
F	3.8	1.4-10.0	43	16-36	0.8	0.1		6
Pb	<0.1	<0.4	0.4	<0.3	0.3	3.5	0.1	
Li							0.4-2.9	1
Mn							0.2	
Hg		0.04		0.005				<0.01
Mo	3	0.1-0.3		0.1-0.5	0.3	0.7	<0.1-0.5	0.1
Ni							0.1-0.4	
Se	<1	1.5-11.0	7.9	3.9-8.3	0.2		0.4-4.4	0.1 (0.8)
Ag	<0.2				<0.2	0.4	<0.1	
Sr							<0.1-0.8	
Th							0.1-1.7	
Zn	1.0	0.2-1.1	1.5	0.1-8.5	0.5	0.6		(2.0)

Sources:

[a] DOE/EV-0086, June 1980.

[b] Jackson & Jackon, 1982.

[c] DRI, June, 1977.

TABLE 3.3-8. COMPOUNDS IDENTIFIED IN PARAHO DIRECT OIL SHALE WASTEWATERS[a]

Compounds	
Total Organic Carbon (ppm)	41,900
Toluene	
Phenol	
o-Cresol	
m-Cresol	
p-Cresol	
C_2-Phenol	
C_3-Phenol	
2,6-Dimethylphenol	
3,5-Dimethylphenol	
Methoxyphenol	
Naphthalene	
2-Methylnaphthalene	
C_2-Naphthalene	
2-Methylpyridine	x
4-Methylpyridine	x
2,3-Dimethylpyridine	
2,4-Dimethylpyridine	x
2,5-Dimethylpyridine	x
2,6-Dimethylpyridine	x
2-Ethylpyridine	
C_2-Pyridines	x
2,4,6-Trimethylpyridine	x
C_3-Pyridines	x
4-(n-propyl)pyridine	
C_4-Pyridines	x
4-(3-pentyl)pyridine	x
C_5-Pyridines	x
Aniline	x
3-Methylaniline	
N-methylaniline	x
N,N-dimethylaniline	x
N-ethylaniline	x
2,4-Diethylaniline	x
N,N-diethylaniline	x
Quinoline	x
Isoquinoline	x

(continued)

TABLE 3.3-8 (continued)

Compounds	
2-Methylquinoline	x
3-Methylquinoline	x
7-Methylquinoline	x
2,4-Dimethylquinoline	x
2,6-Dimethylquinoline	
2,7-Dimethylquinoline	x
Trimethylquinoline	
Acridine	x

[a] Compounds marked with "X" were identified in each sample. Those not marked are not necessarily absent.

Source: Engineering Science, June 1983

TABLE 3.3-9. PARAHO DIRECT RECYCLE GAS LINE DRAIN[a] (ppm)

Analyses	CE-TEMPO 9-09-77	GSRI 12-13-77	PAR 1-04-78	PAR 6-01-78
Aluminum		0.2	<1	<1
Arsenic	10.3	0.9	<2	<2
Barium	<0.1	0.1	<0.5	<0.5
Boron		<0.02	<20	<20
Cadmium		<0.01	≤0.01	<0.05
Calcium	13.7	4	2.8	21
Chromium	<0.03	0.02	0.01	0.00
Copper	0.2	0.9	0.09	<0.05
Iron	1.5	2	2.2	0.9
Lead	0.2	0.04	<0.5	<1
Magnesium	29.5	1	20	30
Mercury		4.8 ppb	<5	<7
Molybdenum		0.04	≤0.2	2
Potassium	2.4		0.82	2.1
Selenium	1.8	0.1	2	<1
Silver		<0.01	0.7	1.0
Sodium	27.6		11	60
Silicon		3	<2	7
Zinc	0.1	0.6	0.02	0.03
Alkalinity as $CaCO_3$			19,400	25,000
Carbonates			13,410	2,514
Carbon, total			7,400	6,970
Carbon, organic			3,740	6,280
Chemical oxygen demand			1,600	1,850
Chloride		0.5	750	32
Cyanide			60.0	5.3
Fluoride	1.6	≃0.07	0.96	<0.04
Hydrogen, total			106,900	
Nitrogen, total			4,900	5,910
Nitrogen, ammonia			5,960	6,985
Nitrogen, nitrate			<0.02	<0.1
pH	8.9		8.9	9.0
Phenol			19.2	67
Phosphate, total			<1	<0.1
Total suspended solids			9	<0.02
Total dissolved solids[b]			3.3	11.9/9.3
Sulfur, sulfate	1540		1,400	460
Sulfur, sulfide			<1	<0.01
Sulfur, total			≤500	2,570

---

[a] After oil separation.

[b] Values reported are for TDS after vacuum evaporation at ambient temperature and after evaporation at 180°C, respectively.

Source: DOE/EV-0086, June 1980

TABLE 3.3-10. CONCENTRATIONS IN RCRA AND WATER SHAKE TEST EXTRACTS - PARAHO DIRECT SPENT SHALES

Parameter	Units	RCRA	ASTM
pH	-	9.27	12.05
EC	μmhos/cm @ 25°	4600	2800
ALK	mg/L	2593	398
H_2CO_3	mg/L	3.5	<0.001
HCO_3	mg/L	2723	5.0
CO_3	mg/L	217	236
TDS	mg/L	6220	1425
F	mg/L	-	13.5
Cl	mg/L	28.8	7.2
PO_4	mg/L	<0.05	<0.1
NO_3	mg/L	1.75	3.5
SO_4	mg/L	220	536
Zn	mg/L	<0.001	0.0003
Fe	mg/L	0.020	<0.005
Co	mg/L	0.044	<0.005
Li	mg/L	0.503	0.944
V	mg/L	0.018	0.035
NH_3	mg/L	0.161	2.2
B	mg/L	0.333	0.513
Cd	mg/L	<0.001	<0.001
Be	mg/L	<0.0005	<0.0005
Mg	mg/L	484	0.5
P	mg/L	0.49	0.3
Si	mg/L	4.0	2.3
Mo	mg/L	<0.05	<0.05
Mn	mg/L	0.016	0.002
Ni	mg/L	<0.05	<0.005
Na	mg/L	37	145
Cu	mg/L	0.019	0.002
Al	mg/L	3.0	<0.02
Ca	mg/L	724	266
Ba	mg/L	0.915	0.157
K	mg/L	6.5	31
Cr	mg/L	<0.10	<0.005
Sr	mg/L	8.4	5.0
Pb	mg/L	<0.010	<0.01
Ag	mg/L	<0.002	0.003
Ti	mg/L	<0.005	<0.005
Se	mg/L	<0.020	<0.020
As	mg/L	0.010	<0.01
Hg	mg/L	<0.001	<0.001

Source: EPA-600/D-84-228, 1984

TABLE 3.3-11. LEACHABLE MASS AS INDICATED BY THE ASTM PROPOSED WATER SHAKE EXTRACTION TEST FOR PARAHO DIRECT SPENT SHALES - mg/g

Parameter	Paraho
Na	0.580
Ca	1.064
Mg	0.002
SO_4	2.144
Cl	0.029
F	0.054
B	0.002
Mo	0.003
Al	0.005
TDS	5.700

Source: EPA-600/D-84-228, 1984

TABLE 3.3-12. COLUMN LEACHING EFFLUENT CONCENTRATIONS FOR PARAHO DIRECT SPENT SHALES

$\frac{vt}{L}$	Ca	Na	Cl mg/L	SO_4	F	pH
0.022	610	1,500	49	3,840	21.0	11.55
0.032	605	1,445	47	3,805	22.2	11.60
0.047	610	1,385	47	3,735	21.9	11.66
0.070	625	1,305	42	3,695	22.0	11.73
0.088	625	1,280	39	3,525	22.6	11.78
0.105	640	1,165	35	3,485	21.0	11.81
0.128	660	1,095	33	3,320	21.0	11.86
0.151	635	1005	31	3,270	21.5	11.89
0.167	635	955	30	3,180	22.0	11.91
0.178	610	965	27	3,185	20.4	11.83
0.190	650	935	26	3,175	20.9	11.94
0.202	605	895	26	3,085	21.4	11.95
0.220	635	875	23	3,060	21.1	11.99
0.244	670	830	24	3,065	21.8	12.02
0.263	660	785	27	2,975	21.8	12.01
0.275	670	780	32	2,930	22.5	12.03
0.294	680	760	30	2,890	21.9	12.06
0.312	620	705	23	2,890	21.6	11.96
0.353	685	640	25	2,815	14.2	12.06
0.367	665	595	24	2,605	12.4	12.10
0.412	700	565	26	2,615	14.4	12.13
0.423	655	525	21	2,530	14.5	12.07
0.473	715	490	17	2,500	12.7	12.14
0.483	710	460	19	2,395	12.8	12.17
0.606	700	430	18	2,390	12.5	12.21
0.644	730	370	14	2,290	11.5	12.24
0.726	660	340	16	2,205	12.4	12.27
0.836	680	305	13	2,105	11.4	12.31
0.918	670	285	14	2,045	11.4	12.35
1.642	560	140	9	1,500	10.2	12.46
1.978	380	100	6	1,000	8.1	12.57
2.177	390	105	6	860	8.3	12.60

Key

$K = 4.6 \times 10^{-4}$ cm/s

$\frac{vt}{L}$ = pore volume.

Source: EPA-600/D-84-228, 1984

TABLE 3.3-13. INORGANIC COMPOSITION OF PARAHO DIRECT SPENT SHALE LEACHATES PRODUCED DURING FIELD LYSIMETER STUDIES, (mg/L)

	Lysimeter[a] Percolate Colorado Shale (Garland et al., 1979)	Lysimeter[a] Runoff Colorado Shale (Kilkelly et al., 1981)
Al	0.0005 - 0.1	-
As	0.007 - 0.08	-
B	0.5 - 3	-
Ba	0.03 - 0.55	-
Br	-	-
Ca	140 - 530	7 - 10
Cd	-	-
Cl	70 - 2,200	<4
CO_3	-	-
Cr	<0.001 - 0.02	-
Cu	<0.001 - 0.07	-
DOC	<2 - 400	-
EC, µmhos/cm	8,000 - 30,000	70 - 170
F	3 - 13	-
Fe	<0.01 - 0.3	-
HCO_3	-	18 - 50
K	320 - 1,230	4 - 5
Li	6 - 20	-
Mg	0.2 - 140	3 - 14
Mn	<0.01 - 0.075	-
Mo	1.2 - 9.5	-
Na	1,500 - 10,400	2 - 5
Ni	<0.005 - 0.04	-
NH_4	<1 - 11	-
NO_3	<0.1 - 6	-
NO_2	0.001 - 4	-
Pb	-	-
PO_4	-	-

(continued)

TABLE 3.3-13 (continued)

	Lysimeter[a] Percolate Colorado Shale (Garland et al., 1979)	Lysimeter[a] Runoff Colorado Shale (Kilkelly et al., 1981)
Rb	-	-
Se	0.0005 - 0.04	-
Si	5 - 16	-
SO_4	3,000 - 20,000	5 - 14
Sn	<0.04	-
Sr	4 - 13	-
TDS	-	-
TOC	2 - 429	-
U	<0.0003 - 0.003	-
V	0.1 - 0.45	-
Zn	0.005 - 1.1	-
pH	6.9 - 11.5	-
Bulk density, g/cm^3	1.55	
Solid-to-liquid ratio, g/mL	-	
Contact time, min	-	
Particle size, d_{50}	-	
Number of replicates	NA	

[a] Anvil Points lysimeter, high elevation site. Runoff values are for spring snowmelt. The first reported value for runoff is from spent shale with 20-cm soil cover and the second value is for runoff from preleached, bare spent shale.

Source: Fox, July 1983

3.4 PARAHO INDIRECT HEATING MODE OIL SHALE RETORTING

3.4.1 Retorting Operation

The Paraho indirect mode of operation is basically the same as the direct mode (Section 3.3.1), using the same-sized raw shale feedstock, the same retort, and much of the same auxiliary equipment. In the indirect mode, the air blowers are replaced with external heaters. Internal combustion is eliminated. The offgas is reduced in volume with an increase in the high heating value (HHV) to 900 Btu/SCF.

The principal zones within the retort are essentially the same as the direct mode, except that in the indirect mode, the combustion zone becomes the heating zone (Figure 3.4-1). Since there is no internal combustion, the organic carbon remaining on the shale after retorting is not diminished and is about 2%.

Because of changes in the nature and flows of the recycle gas, the temperatures of both the offgas and retorted shale are somewhat hotter for the indirect mode. Both the retorted shale and the offgas temperatures average approximately 300°F.

The Paraho indirect mode has not been tested as extensively as the direct mode. Thus, the indirect mode data are quite limited and, since the Paraho retort had not been operated for extensive periods of time, much of the samples and data that have been obtained represent somewhat unstable start-up or shutdown conditions. No extensive engineering designs have been made for a commercial-size facility using Paraho indirect mode retorting technology.

3.4.2 Solid Wastes

Although no block-flow diagram is available for the Paraho indirect mode process, the diagram provided for the Paraho direct mode process (see Figure 3.3-2 in Section 3.3.2) can be used to obtain good estimates of processed shale and other solid wastes for a commercial facility using Paraho indirect mode retorting technology.

Raw shale rates, fines storage, and dusts will be approximately the same for both processes. It is likely that the indirect mode process will produce a slightly higher rate of retorted shale because of the lower carbonate decomposition and higher organic carbon content, but the overall rate should not increase by more than 1 to 2%. Because of this slight increase in the retorted shale rate and the likelihood of increased temperatures, water consumption for dust control and emergency temperature control would also increase.

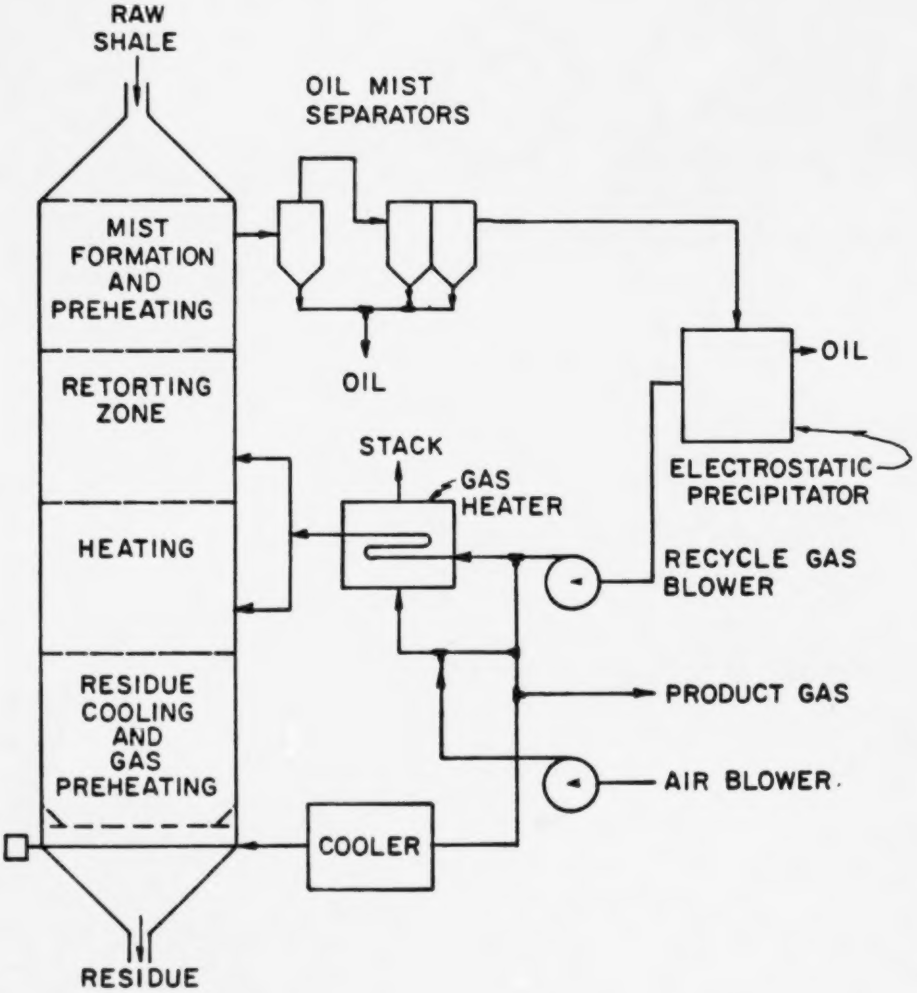

RAW SHALE
OIL MIST SEPARATORS
MIST FORMATION AND PREHEATING
RETORTING ZONE
HEATING
RESIDUE COOLING AND GAS PREHEATING
OIL
OIL
ELECTROSTATIC PRECIPITATOR
STACK
GAS HEATER
RECYCLE GAS BLOWER
PRODUCT GAS
AIR BLOWER
COOLER
RESIDUE

Figure 3.4-1. Paraho indirect mode process flow diagram. Source: EPA-600/7-79-075, 1979.

As there is no information available for other solid wastes produced by a facility based upon Paraho indirect mode technology, a general estimate of these wastes is available from information based upon the Paraho direct mode process (see Table 3.3-1 in Section 3.3.2).

The product gas will experience the biggest single change between the Paraho indirect mode and the Paraho direct mode processes. The offgas volume decrease is largely offset by increases in concentrations. Thus, the overall energy (MBtu/hr), the sulfur production, ammonia production and the estimated rates for catalysts, sludges, non-marketable byproducts, and other solid wastes will be essentially the same.

3.4.3 Characteristics of Solid Wastes

Except for retorted shale, the characteristics of Paraho indirect process solid wastes should be quite similar to Paraho direct process solid wastes. Available characterization data for Paraho indirect retorted shale are presented in Tables 3.4-1 to 3.4-3. Available information regarding process water characteristics produced from the Paraho indirect mode technology is presented in Tables 3.4-4 and 3.4-5. The limited amount of data on leachate characteristics produced from experiments using retorted shale produced by the Paraho indirect mode is presented in Table 3.4-6.

TABLE 3.4-1. PARAHO INDIRECT RETORTED SHALE CHARACTERISTICS[a]

A. Size Classification

Unified Soil Classification System

Designation	Size, mm	Weight percent
Cobble	+38.1	-
Gravel	4.76 - 38.1	52.4
Sand	0.074 - 4.76	31.9
Silt	0.005 - 0.074	13.3
Clay	-0.005	2.4

B. Density

Compactive effort ft.-lb/cu. ft.	Water Added Density, lb/cu. ft. None	 Optimum, 22 wt. %
Light, 6,200	89.0	93.9
Std. Proctor, 12,375	94.4	98.8/99.2
Heavy, 56,250	102.1	105.8

C. Strength

Days curing	Compressive strength, psi
28	11.8
60	15.3
120	10.8

D. Permeability

Compactive effort ft.-lb/cu. ft.	Loading psi	Permeability, ft/yr No water	 Optimum water
Light, 6,200	50	71	-
	100	52	-
	200	30	-
Heavy, 56,250	50	2	-
	100	2.5	-
	200	2.4	-

---

[a] Holtz, 1976.

TABLE 3.4-2. PARAHO INDIRECT RETORTED SHALE CHEMICAL COMPOSITION

Major component[a]	Concentration, wt. %
Ash	79.4, 79.1
Min CO_2	18.1
Organic C	1.8
Si	10.8
Al	4.2
Fe	1.9
Ca	10.9
Mg	3.9
S	0.7
Na	1.7
K	2.0

Trace components[b]	Concentration, ppm
Be	0.7
Hg	0.03
Cd	-
Sb	0.8
Se	0.2
Mo	10
Co	16
Ni	14
Pb	11
As	18
Cr	66
Cu	26
Zr	62
B	18
Zn	21
V	88
Mn	272
F	450

[a] WCC (Holtz), 1976.

[b] TRW, 1977.

TABLE 3.4-3. COMPOSITION OF PARAHO INDIRECT SPENT OIL SHALES

Component	Weight, %
SiO_2	23.1
CaO	15.3
MgO	6.5
Al_2O_3	8.0
Fe_2O_3	2.7
Na_2O	2.3
K_2O	2.4
SO_3	0.7
P_2O_5	-
Mineral CO_2	18.1
Organic C	1.84
Inorganic C	4.95
Texture	silty gravel
pH	10.9

Source: EPA-600/2-80-205a, 1980

TABLE 3.4-4. PARAHO INDIRECT PROCESS WATER COMPOSITION

Element	μg/mL
Lead	0.2
Mercury	<0.01
Cesium	0.01
Barium	2.0
Molybdenum	0.1
Strontium	3.0
Bromine	0.009
Selenium	0.1
Arsenic	1.0
Gallium	<0.02
Zinc	0.4
Copper	0.2
Nickel	0.2
Cobalt	<0.04
Germanium	<0.05
Iron	5.0
Manganese	0.3
Chromium	0.3
Vanadium	0.03
Titanium	0.3
Scandium	<0.05
Calcium	>10
Potassium	>10
Chlorine	2.0
Sulfur	>10
Phosphorus	5.0
Silicon	>10
Aluminum	0.8
Magnesium	>10
Sodium	>10
Fluorine	7
Boron	5.0
Lithium	1.0

Source: EPA-600/2-80-205a, 1980

TABLE 3.4-5. INORGANIC ANALYSIS OF CONDENSATE STREAMS FROM THE PARAHO INDIRECT PROCESS

Parameter	mg/L
Cations:	
Calcium	39.16
Magnesium	<0.1
Sodium	0.29
Potassium	0.18
Ammonium, NH_4^+	13,440-calc.
Anions:	
Carbonates	3,030-calc.
Bicarbonates	6,280-calc.
Sulfate	1.65
Sulfide	390
Chloride	TR
Fluoride	0.10
Nitrate	1.0
Nitrite	<0.002
Nutrients:	
NH_3-N	16,800-calc.
Phosphate, total	0.75
Gross parameters:	
BOD	4,850
COD	17,100
TOC	9,800-36,900
TIC	1,600
Oil and grease	33.3
Solids, total	429
Solids, upon evaporation	406
Total alkalinity	12,900
Hardness	98-calc.
Phenols	42
pH	9.5

Source: EPA-600/2-80-205a, 1980

TABLE 3.4-6. COMPOSITION OF BATCH GENERATED LEACHATE FROM PARAHO INDIRECT RETORTED SHALE

Element	mg/L
Al	<0.03
Ca	4.3
Fe	0.04
K	3.3
Mg	1.8
Si	8.5
Na	65
SO_4	25
CO_3	1.4
HCO_3	<0.1
Cl	44
pH	10.9

Source: Holtz, 1976.

3.5 OCCIDENTAL MODIFIED *IN SITU* OIL SHALE RETORTING

3.5.1 Retorting Operation

The recovery of shale oil by the Occidental modified *in situ* (MIS) process involves the underground pyrolysis of large chambers of rubblized shale [Fox, July 1983]. These chambers are constructed by mining out about 20% of the volume of the retort and blasting the balance so that the entire chamber is filled with fractured rock. A commercial-sized retort will measure about 333 ft by 166 ft in cross section and 400 ft high. Oil is recovered from such a retort, shown in Figure 3.5-1, by initiating combustion at the top of the retort with an external fuel supply and propagating the reaction zone, which consists of a pyrolysis zone and a trailing combustion zone, down the bed of rubblized with input gas. The volatile hydrocarbons condense in the cool region at the bottom of the retort and are pumped to the surface.

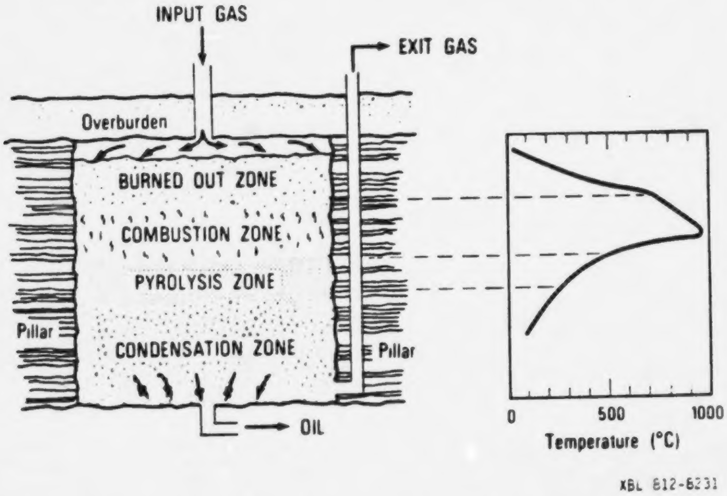
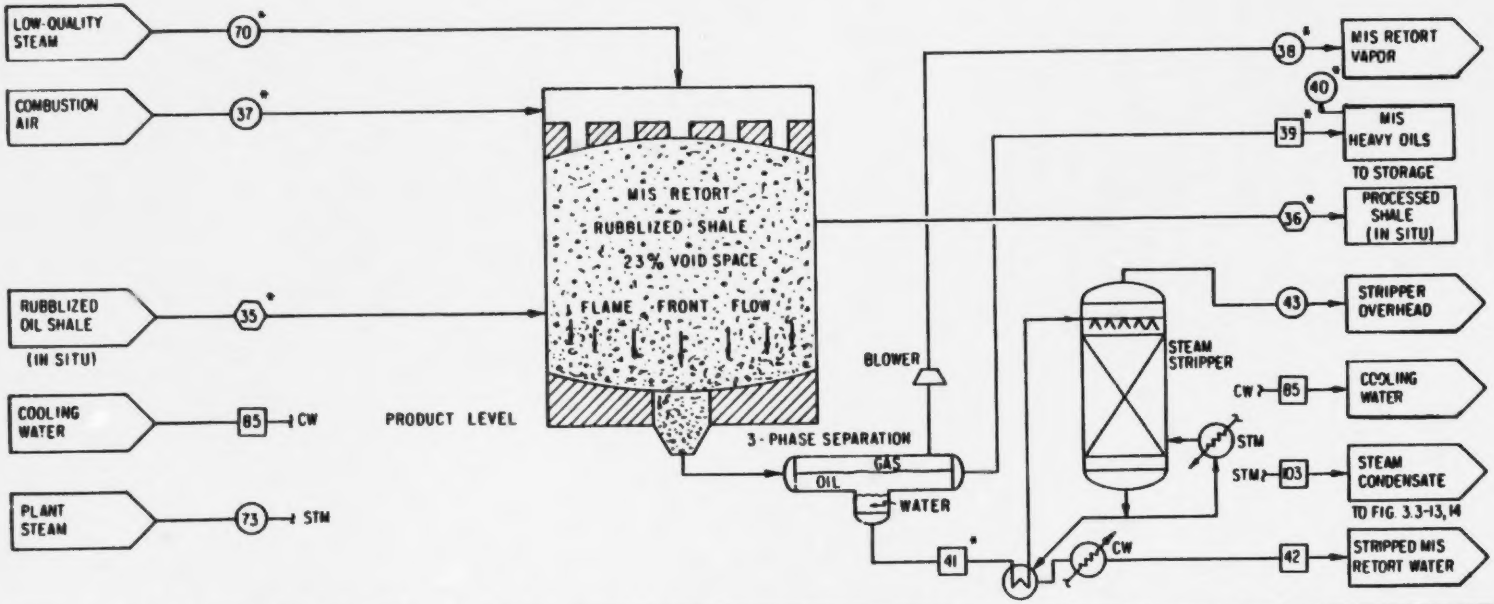


Figure 3.5-1. Schematic of the Occidental modified *in situ* retorting process.

Source: Fox, July 1983.

Occidental has tested eight experimental retorts at Logan Wash, Colorado. Leaching studies have been conducted on materials from Retort 3. Retort 3 was operated between February and July of 1975 in air-recycle gas mode. Yield was around 60% Fischer Assay. This retort was cored in December 1978, and the spent shales have been characterized and subjected to leaching studies.

Figure 3.5-2 presents a conceptual illustration of a rubblized MIS retort [EPA-600/8-83-004, 1983]. In the operation of an MIS retort, air and steam (streams 37 and 70) are admitted at the top


LOW-QUALITY STEAM
70*
COMBUSTION AIR
37*
RUBBLIZED OIL SHALE (IN SITU)
35*
COOLING WATER
85
CW
PLANT STEAM
73
STM
PRODUCT LEVEL
MIS RETORT
RUBBLIZED SHALE
23% VOID SPACE
FLAME FRONT FLOW
3-PHASE SEPARATION
GAS
OIL
WATER
BLOWER
41*
STEAM STRIPPER
CW
STM
38*
MIS RETORT VAPOR
40*
39*
MIS HEAVY OILS
TO STORAGE
36*
PROCESSED SHALE (IN SITU)
43
STRIPPER OVERHEAD
85
COOLING WATER
103
STEAM CONDENSATE
TO FIG. 3.3-13, 14
42
STRIPPED MIS RETORT WATER

STREAM NO	35*	36*	37*	38*	39*	40*	41*	42	43	70*	73	85	103
STREAM IDENTITY	RUBBLIZED OIL SHALE (IN SITU)	PROCESSED SHALE (IN SITU)	COMBUSTION AIR	MIS RETORT VAPOR	MIS HEAVY OILS	MIS OIL STORAGE HC EMISSION	MIS RETORT WATER	STRIPPED MIS RETORT WATER	STRIPPER OVERHEAD	LOW-QUALITY STEAM	PLANT STEAM	COOLING WATER	STEAM CONDENSATE
FLOW RATE: 10^3 ACFM 10^3 lb/hr gpm	15,083	11,421	6508	4470 10,998.3	911 1810	(included in # 28) N.D	611.5 1200(AV.)	513.9 1013(AV)	97.6	1511.3	90	N.D.	180
TEMP., °F	AMB	N.D	AMB	150	150	AMB	150	135	200	400	300	AMB	120
PRESSURE, psig	AMB ←								← AMB	265	85	AMB	AMB

SOURCE: DRI based on Occidental Oil Shale, Inc. and Tenneco Shale Oil Co., April 1981

* Indicates streams that contact the environment.

Figure 3.5-2. Occidental MIS Retorting, Oil/Water Separation and Steam Stripping.

Source: EPA-600/8-83-004, 1983

through several openings which connect the retort air level to the top of the rubblized shale. The steam is produced from process waters, using kettle evaporators and Lurgi waste heat recovery boilers. Steam promotes the water/gas reaction and provides a means of controlling the combustion zone temperature. Retort start-up is accomplished through introduction of hot inert gas. When the temperature of the broken rock at the top of the retort is high enough, air is introduced to initiate combustion.

An operating retort contains four major zones. In the first, or preheat zone, the air/steam feed gas is preheated through contact with hot processed shale. The heated gas then reaches a combustion zone where oxygen is consumed by burning residual carbon in the processed shale. Below the combustion zone is the retorting zone where hot combustion gases heat the raw shale rubble to approximately 900°F, and the retorting process commences. During retorting, the kerogen is pyrolyzed to produce gas, oil and oil vapor, and solid residue with residual carbon. The shale oil moves downward by gravity and precedes the advancing combustion front by six to ten feet. In the final zone, the combustion and retorting gases are cooled as they flow downward, condensing most of the vaporized oil. During the early stages of the burn, when the rock is still cool, some water is also condensed.

Oil, water, and retort gas exit the bottom of the MIS retort and undergo separation in a three-phase separation sump located underground. Heavy oils (stream 39) obtained from this sump are pumped to storage. The retort water (stream 41) is also pumped to the surface and steam stripped to remove volatile compounds. The overhead vapors (stream 43) are sent to the Phosam-W unit, while the stripped water is used in the production of low-quality steam to be injected back into the MIS retorts. The retort gas mixture (stream 38) consists of light hydrocarbons from shale pyrolysis, carbon dioxide and water vapor from the combustion of carbonaceous residue, water vapor from steam injection, carbon dioxide from the decomposition of inorganic carbonate (primarily dolomite and calcite), and nitrogen from the combustion air. In addition, the gas contains ammonia and sulfur-bearing gaseous products such as H_2S and COS. The gases are drawn to the surface by large blowers and fed to an absorption/cooling oil recovery unit.

3.5.2 Solid Wastes

Table 3.5-1 presents an inventory of solid and liquid waste streams. From a commercial size development with 229 retorts operating simultaneously, each 120 ft x 120 ft x 250 ft and containing oil shale with an average Fischer assay of 15 gpt, the Occidental modified *in-situ* process will generate among other products the following: Mined rock - 56,685 tons per calender day; Wastewater - 1,458 gpm [EPA-600/7-79-075, 1979].

3.5.3 Characteristics of Solid Wastes

Compositions of solid and liquid waste streams are shown in Table 3.5-2. Available data on spent shale are presented in Tables 3.5-3 and 3.5-4. Analytical data on core samples are given in Tables 3.5-5 and 3.5-6. Data on steam boiler blowdown and wastewaters are shown in Tables 3.5-7 to 3.5-9. Finally, various leachate data are presented in Tables 3.5-10 to 3.5-12.

TABLE 3.5-1. INVENTORY OF SOLID AND LIQUID WASTE STREAMS FOR OCCIDENTAL MIS PROCESS (69,000 BPSD Plant Size)

Stream number	Description of stream	Mass flow, gpm (10^3 lb/hr)	Components of concern	Mass flow of component, lb/hr	Remarks[b]
36[a]	MIS processed shale (in-place)	(11,421)	Leachable salts	N.D.[c]	Groundwater infiltration may cause some leaching, hence contamination of the natural subsurface waters.
41[a]	MIS retort water (average-maximum)	1200-4520 (611.5-2303.3)	NH_3 H_2S Dissolved inorganics Dissolved organics	780-2,988 60-226 5,130-19,320 2,772-10,442	
42	Stripped MIS retort water (average-maximum)	1013-3816 (513.9-1935.6)	NH_3 Dissolved inorganics Dissolved organics	30-114 5130-19,320 2,218-8,354	Low-quality steam is produced from the stripped retort water. The volatile components end up in the steam used in the MIS retorts. NH_3 may be recovered in the MIS gas condensate. The nonvolatile components are concentrated in the kettle evaporators.
-	MIS gas condensate	3716 (1919.9)	NH_3 H_2S Dissolved organics Dissolved inorganics	26,650 240 1,534 520	Steam stripping removes the volatile components. The nonvolatile matter is concentrated in the kettle evaporators and eventually disposed of with the processed shale.
103	Steam condensate from MIS retort water steam stripper	180	--[d]	--	
-[a]	Blowdown from MIS humidified air coolers (Case Study B)	739	Dissolved and suspended solids	N.D.	The cooler blowdown is equalized with other plant effluents and used for processed shale moisturizing.

[a] Indicates streams that come into contact with environment.

[b] The remarks indicate the stream disposition. The controls and treatments applied to the streams are those specified for the Cathedral Bluffs Project.

[c] N.D. - not determined.

[d] Dashes (--) - indicate no known components of concern.

Source: EPA-600/8-83-004, 1983

TABLE 3.5-2. COMPOSITIONS OF SOLID AND WASTE STREAMS FOR OCCIDENTAL MIS PROCESS (69,000 BPSD Plant Size)

Stream number	Stream description	Mass flow, 10^3 lb/hr	Components,[a] 10^3 lb/hr					
			H	O	N	C	S	H_2O
36[b]	MIS process shale	11,421	0	0	0	274	71	0
		Mass flow, gpm (10^3 lb/hr)	Components, lb/hr					
			CO_2	NH_3	H_2S	TDS & TSS[c]	Organics	H_2O
41[b]	MIS retort water (average-maximum)	1200-4520 (611.5-2303.3)	2,748-10,350	780-2,988	60-226	5,130-19,320	2,772-10,442	600,000-2,260,000
42	Stripped MIS retort water (average-maximum)	1013-3816 (513.9-1935.6)	0	30-114	0	5,130-19,320	2,218-8,354	506,507-1,907,843
-	MIS gas condensate	3716 (1919.9)	33,000	26,650	240	520	1,534	1,857,978
103	Steam condensate from MIS retort water steam stripper	180	0	0	0	0	0	90,000
-[b]	Blowdown from MIS humidified air coolers (Case Study B)	739	0	0	0	N.D.	N.D.	369,500

[a] Elements reported for organic portion of materials, except for sulfur which is total.

[b] Indicates streams that come into contact with the environment.

[c] TDS - total dissolved solids. TSS - total suspended solids.

Source: EPA-600/8-83-004, 1983

TABLE 3.5-3. COMPOSITION OF OCCIDENTAL MIS PROCESSED SHALE

Component	Weight percent	Mass flow, 10^3 lb/hr	Flow, 10^3 lb-moles/hr
Processed shale (in-place)	100.00	11,421	-
Carbon (organic)	2.40	274	23
Sulfur (total)	0.62	71	2.2

Source: EPA-600/8-83-004, 1983. 69,000 BPSD Plant Size

TABLE 3.5-4. BORON AND FLUORIDE IN OXY RETORT 3E SPENT SHALE

Sample number	Depth, ft.	F[a] µg/g ±10%	B[b] µg/g ±10%
1	442 - 445	470	210
3	457 - 460	530	140
4	460 - 463	680	110
14	483 - 485	1,200	275
15	483.5 - 485.5	1,100	210
17	500 - 506	2,600	470
18	506 - 515	2,300	550

[a] F - gas diffusion-colorimetric

[b] B - colorimetric (Azomethine-H).

Source: DOE/EV-0078, May 1980

TABLE 3.5-5. MINERALOGICAL ANALYSES FOR SELECTED SAMPLES OF OXY REPORT 3E SPENT SHALE CORE

	No. 5	No. 16
Mean depth (ft)	464.5	493
Major mineral (s)	Calcite	Akermanite
Minor mineral (s)	Diopside α-quartz Aragonite Kalsilite	Diopside
Trace mineral (s)	Akermanite	Kalsilite 2 Unidentified phases

Source: DOE/EV-0078, May 1980

TABLE 3.5-6. ANALYSIS OF CORE SAMPLES FROM OXY RETORT 3E PRELIMINARY DATA[a]

Element	Average concentration	Element	Average concentration
Al[b]	4.7 ± 2%	Mg[b]	5.8 ± 0.6%
As[b]	26 ± 2 ppm	Mn[d]	520 ± 52 ppm
B[c]	256 ppm	Mo[d]	10 ± 1 ppm
Ba[b]	593 ± 60 ppm	Na[b]	1.26 ± 0.03%
Ca[d]	19 ± 1.4%	Ni[d]	29 ± 3 ppm
Cs[b]	5.0 ± 0.5 ppm	Pb[d]	26 ± 3 ppm
Cu[d]	44 ± 4.4 ppm	S[d]	0.45 ± 0.07%
Fe[b]	2.43 ± 0.07 ppm	Si[d]	19 ± 2%
Hg[e]	41 ± 6.2 ppb	Sr[d]	1100 ± 110 ppm
K[b,d]	3.0 ± 0.3%	Ti[d]	0.26 ± 3%

[a] Average of 18 samples composited from 5 foot intervals. Mean sample depth = 476 ft.

[b] Neutron activation analysis.

[c] DC Plasma Emission Spectroscopy.

[d] X-ray fluorescence.

[e] Flameless atomic absorption.

Source: DOE/EV-0078, May 1980

TABLE 3.5-7. OXY RETORT 6 STEAM BOILER BLOWDOWN Collected - March 6, 1979 (in ppm except as noted)

	NAA
Aluminum	<4.01
Arsenic	2.8 ± 0.2
Antimony	0.09 ± 0.01
Bromine	6.8 ± 0.2
Calcium	<80
Chlorine	2,220 ± 25
Chromium	<0.1
Cobalt	<0.01
Iron	<5
Magnesium	120 ± 20
Manganese	<0.2
Molybdenum	7.3 ± 0.6
Nickel	<1
Nitrogen	216 ± 10
Selenium	0.15 ± 0.02
Sodium	14,100 ± 100
Sulfur (%)	0.50 ± 0.08
Uranium	0.22 ± 0.03
Vanadium	<0.01
Zinc	±0.3

Source: DOE/EV-0078, May 1980

TABLE 3.5-8. COMPOUNDS IDENTIFIED IN OCCIDENTAL OIL SHALE RETORT WASTEWATERS

Total organic carbon	2,300 ppm
Toluene	x
Phenol	x[a]
o-Cresol	x
m-Cresol	x
p-Cresol	x
C_2-Phenol	x
C_3-Phenol	
2,6-Dimethylphenol	
3,5-Dimethylphenol	x
Methoxyphenol	
Naphthalene	
2-Methylnaphthalene	
C_2-Naphthalene	
2-Methylpyridine	
4-Methylpyridine	
2,3-Dimethylpyridine	
2,4-Dimethylpyridine	
2,5-Dimethylpyridine	
2,6-Dimethylpyridine	
2-Ethylpyridine	
C_2-Pyridines	
2,4,6-Trimethylpyridine	x
C_3-Pyridines	
4-(n-propyl)pyridine	
C_4-Pyridines	
4-(3-pentyl)pyridine	
C_5-Pyridines	
Aniline	x
3-Methylaniline	
N-methylaniline	
N,N-dimethylaniline	
N-ethylaniline	
2,4-Diethylaniline	
N,N-diethylaniline	x
Quinoline	x
Isoquinoline	x

(continued)

TABLE 3.5-8 (continued)

Total organic carbon	2,300 ppm
2-Methylquinoline	x
3-Methylquinoline	x
7-Methylquinoline	x
2,4-Dimethylquinoline	x
2,6-Dimethylquinoline	
2,7-Dimethylquinoline	
Trimethylquinoline	
Acridine	

[a] Compounds marked with "X" were identified in each sample. Those not marked are not necessarily absent.

Source: ESI, June 1983

TABLE 3.5-9. OXY RETORT 6 PRODUCT WATER ANALYSIS RESULTS (ppm)

	NAA	XRF	Other
Aluminum	<1		
Antimony	0.018 ± 0.008		
Arsenic	1.32 ± 0.06	0.87 ± 0.01	
Boron			12.6 ± 0.5[a] 13.1 ± 0.03[b]
Bromine	0.34 ± 0.06	0.28 ± 0.04	
Calcium		0.72 ± 0.43	
Chlorine	232 ± 9	183 ± 8	
Chromium	<0.8	<0.07	
Cobalt	<0.2	<0.02	
Copper	<4	0.03 ± 0.01	
Fluoride			34.8 ± 1.0[c]
Gallium		<0.01	
Iron	<120	0.19 ± 0.02	
Lead		<0.04	
Lithium			1.80 ± 0.05[e]
Magnesium	<30		
Manganese	<0.1	<0.04	
Mercury			<0.02[d]
Molybdenum	0.3 ± 0.1		0.257[a]
Nickel	<0.3	<0.02	
Nitrogen			1500 ± 100
Potassium		36 ± 2	
Selenium	0.04 ± 0.01		
Silicon		<160	
Sodium	2810 ± 20		
Strontium		0.57 ± 0.08	
Sulfide			112 ± 15
Sulfur	3100 ± 870	2720 ± 150	
Titanium		0.53 ± 0.07	
Uranium	<0.06		
Vanadium	<0.04	<0.12	
Zinc	<0.2	<0.1	

[a] DC plasma emission spectroscopy.

[b] Colorimetric.

[c] Selective ion electrode.

[d] Cold vapor atomic absorption.

[e] Conventional atomic absorption.

Source: DOE/EV-0078, May 1980

TABLE 3.5-10. CONCENTRATIONS OF DISSOLVED SPECIES IN THE LEACHATE FROM OCCIDENTAL MIS PROCESSED SHALE

Ore sample number	Constituent concentration, mg/L								
	F	B	Mo	As	Se	S_2O_3	SO_4	Ca	TDS
1	1.2	3.5	2.4	0.01	0.02	0	990	16	2,370
2	2.0	2.1	0.9	0.09	0.02	0	2,970	250	4,700
3	6.0	2.6	8.8	0.16	0.10	260	5,340	180	8,250
4	11.0	7.6	5.6	0.03	0.15	210	6,530	920	10,300

Source: EPA-600/8-83-004, 1983

TABLE 3.5-11. CONCENTRATION RANGE OF MACRO IONS FOUND IN THE FIRST FRACTION OF LEACHATES FROM OCCIDENTAL MIS RETORTED SHALE

	Core/samples
Quantity of shale in column (g)	4.0 - 7.7
Column volume collected (v/v_o)	0.28 - 1.11
pH	7.75 - 10.6
Conductivity (µmhos/cm)	1300 - 15,000
Organic C (µg/mL)	152 - 2455
Inorganic C (as CO_3)(µg/mL)	30 - 280
Boron (µg/mL)	1.9 - 46
Calcium (µg/mL)	11 - 513
Magnesium (µg/mL	0.5 - 265
Potassium (µg/mL)	70 - 3360
Sodium ((µg/mL)	370 - 14,400
Lithium (µg/mL)	0.2 - 87
Strontium (µg/mL)	0.7 - 10.8
Silicon (µg/mL)	5.4 - 122
Zinc (µg/mL)	<0.01 - 0.48

Source: DOE/EV-0078, May 1980

TABLE 3.5-12. INORGANIC COMPOSITION OF LEACHATES FROM OCCIDENTAL'S RETORT 3E, LOGAN WASH, COLORADO (mg/L)

	U.S. DOE, 1980 Core 3E1 (PNL data)	Stollenwerk, 1980 Core 3E1	Peterson et al., 1981		
			Core 3E1	Core 3E2	Core 3E3
Al	-	-	<0.02-6.8	0.022-1.22	0.022-1.22
As	-	0.01-0.16	0.005-0.200	<0.002-0.02	<0.002-0.034
B	1.9-46	2.1-7.6	<0.3-6.7	0.262-6.55	0.171-13.0
Ba	-	-	-	0.028-2.80	0.020-0.96
Be	-	-	-	<0.001-<0.006	<0.001-<0.002
Ca	11-513	16-920	6-1,340	3.54-566	1.6-293
Cd	-	-	-	<0.014-<0.081	<0.02-0.03
Co	-	-	<0.04-0.07	<0.002-0.017	<0.01-0.03
Cu	-	-	<0.02-0.04	<0.002-0.017	<0.001-0.012
DOC	152-2,455	-	-	-	-
DIC	30-280	-	-	-	-
EC, µmho/cm	1,300-15,000	3,340-12,170	-	330-2,780	560-6,990
F	-	1.2-11	0.8-22.5	0.3-21	1-31
Fe	-	-	<0.02-4.68	<0.032-0.98	<0.02-0.67
Hg	-	-	-	<0.082-<0.250	<0.1-<0.19
K	70-3,360	-	-	33-215	5.68-358
Li	0.2-87	-	-	0.053-1.97	0.058-1.70
Mg	0.5-265	-	<0.4-37	0.235-18.2	0.004-129.8
Mn	-	-	<0.02-0.13	<0.006-0.019	<0.004-0.021
Mo	-	0.9-8.8	<0.04-0.50	0.293-1.65	0.081-2.34
Na	370-14,400	-	33-600	40-308	24-1,137
Ni	-	-	-	<0.002-0.080	0.014-0.066
Pb	-	-	<0.0005-0.009	<0.042-0.41	<0.03-0.41

(continued)

TABLE 3.5-12 (continued)

	U.S. DOE, 1980 Core 3E1 (PNL data)	Stollenwerk, 1980 Core 3E1	Peterson et al., 1981 Core 3E1	 Core 3E2	 Core 3E3
S_2O_3	-	0-260	-	-	-
Sb	-	-	<0.002-<0.003	-	-
Se	-	0.02-0.15	<0.001-0.05	<0.002-0.010	<0.004-0.075
Si	5.4-122	-	-	5.4-46.2	1.2-63.8
Sn	-	-	-	<0.060-0.30	<0.04-0.13
SO_4	-	990-6,530	-	-	-
Sr	0.7-10.8	-	-	0.080-4.72	0.023-5.68
Tl	-	-	-	<0.054-<0.062	<0.06-<0.14
Ti	-	-	-	<0.008-0.034	<0.002-0.058
W	-	-	-	<0.048-0.99	<0.007-0.82
V	-	-	<0.10-2.63	0.095-1.90	0.017-1.70
Zn	<0.01-0.48	-	<0.003-0.143	<0.5-<0.8	<0.01
pH	7.75-10.6	7.8-9.0	8.3-10.7	8.78-11.60	8.89-11.70
Type of study	Column	Column	Shaker	Shaker	Shaker
Particle diameter	-100 mesh	-100 mesh	-100 mesh	-100 mesh	-100 mesh
Solid-to-liquid ratio	-	-	0.2 g/mL	0.2 g/mL	0.2 g/mL
Contact time	24 hours	31 days	48 hours	48 hours	48 hours
Column description	0.7 x 15 cm glass columns	1.5 x 15 cm plastic columns	-	-	-
Pore volumes	0.28 - 1.11	1	-	-	-

Source: Fox, July 1983

3.6 T^3 OIL SHALE RETORTING

3.6.1 Retorting Operating

The process (NTU/T^3) incorporates the salient features of the NTU batch retorting process developed in the U.S. in the 1920's and improved by the Bureau of Mines and Department of Energy through extensive experiments with 10-ton and 150-ton batch retorts [BLM, February 1983].

The name T^3 was derived from the three major Moroccan oil shale deposits at Timahdit, Tarfaya, and Tangiers [Bouchta et al., 1981]. The process includes significant improvements based on recent technology development including the vertical modified *in-situ* oil shale process.

The T^3 process basically consists of two retorts; retorting and cooling sections as shown in Figure 3.6-1. The air enters into the bottom of the retort charged with hot spent shale. The water is injected into the air stream by fog nozzles or atomizers. The air mixed with water passes through holes in the retort bottom discharge cones. The water in the air is evaporated when it contacts the hot spent shale. The bottom layer of spent shale is cooled and most of the sensible heat contained in the spent shale is recovered in the form of steam. The mixture of air and steam flows through the hot spent shale bed. Since the residual carbon produced from kerogen thermal decomposition is not completely consumed during retorting, the additional heat energy will be recovered by burning the residual carbon in the spent shale.

The cooled spent shale near the retort bottom is discharged and an equal volume of raw shale is loaded at the top of the retort. The process is repeated until the retort is recharged with the raw shale. The mixture of air and steam will heat the raw shale entering into the retort from the top. The water in the raw shale is also evaporated to produce additional steam. The mixture of air and steam exiting the retort being operated in the cooling mode, is introduced into the retort being operated in the retorting mode. The supplemental steam from the topping turbine is mixed with the steam from the retort in the cooling mode, if necessary, to obtain the required steam concentration of the inlet gas into the retort in retorting mode. However, the supplemental steam is not expected to be required.

The product gas leaving the retort in the retorting mode passes through knock-out pots and a gas cooler located before the blower. Because of high water concentration in the product gas, the blower is located after the gas cooler to reduce the actual volume of off-gass to be handled by the blower. The liquid and gas products are collected and separated in a space below the retort bottom. The liquid products flow into the oil and water separator during retorting. The water is subsequently used during the cooling

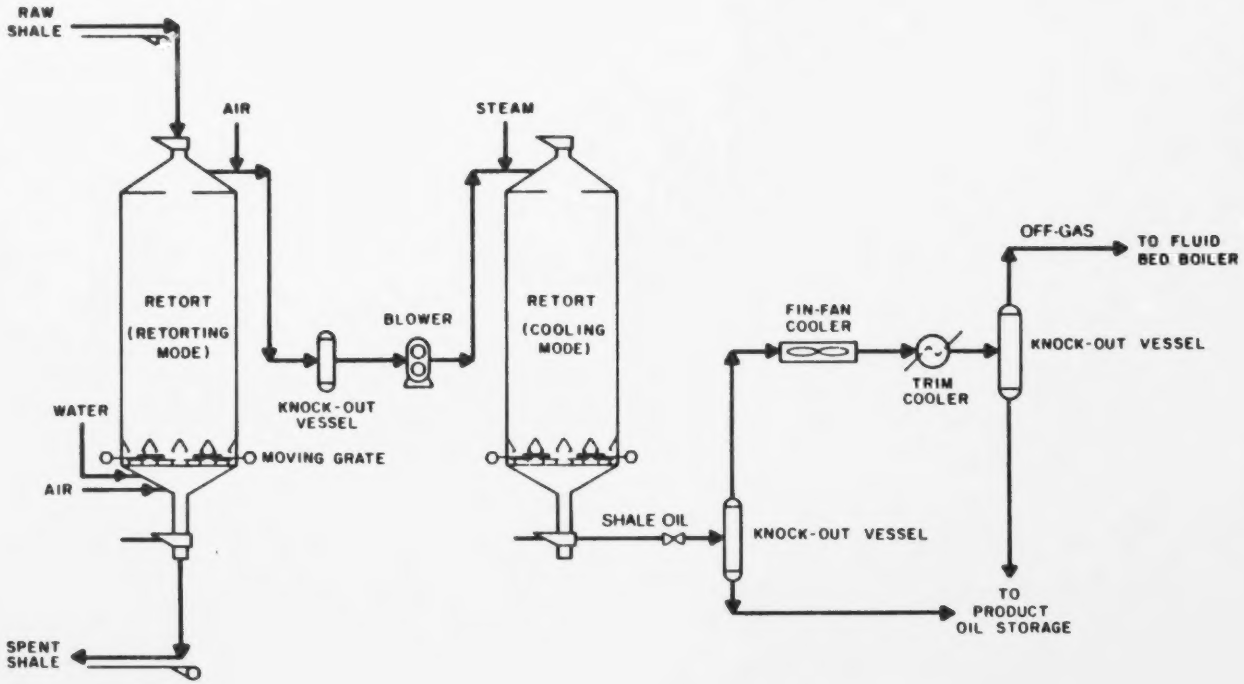

RAW SHALE
AIR
STEAM
RETORT (RETORTING MODE)
BLOWER
RETORT (COOLING MODE)
OFF-GAS
TO FLUID BED BOILER
FIN-FAN COOLER
TRIM COOLER
KNOCK-OUT VESSEL
KNOCK-OUT VESSEL
WATER
AIR
MOVING GRATE
SHALE OIL
KNOCK-OUT VESSEL
TO PRODUCT OIL STORAGE
SPENT SHALE

Figure 3.6-1. T^3 Retorting Process.
Source: BLM, February 1983

of spent shale. The liquid products are separated in the collector into the oil and water phases. The oil is pumped into the heater treater to remove the water. The purging line is provided to remove the combustible gases from the space below the retort bottom when the retorting is complete. The steam introduced into the retort bottom will also generate the hydrogen and carbon monoxide by the reaction of steam with the residual carbon in the spent shale. This gas may be used as a start-up fuel.

Since the major mechanism for transferring the heat energy from hot spent shale to the gas stream is the evaporation of water droplets in the air, it is necessary to carry the water droplets through the spent shale bed. The spent shale absorbs the water, to almost 30% of the spent shale weight, if the temperature is below 200°F. Therefore, it is necessary to discharge the spent shale incrementally from the retort bottom to avoid the water absorption by the spent shale. In addition, the incremental discharge of spent shale will also allow the incremental loading of raw shale into the retort. Because of a large retort height, the batch loading of raw shale may cause a serious damage to the retort wall and may also cause degradation of shale particles. In order to obtain radially even movement of shale, it may be necessary to use multiple vibrating retort bottoms such as bin activators. The charging and discharging cycle is dependent mainly on the air velocity and water injection rate.

In the T^3 process the spent shale is cooled before discharge and the significant amount of sensible heat contained in the spent shale is recovered in the form of steam. A mixture of air and steam instead of air and recycle gas mixture is used for retorting oil shale in the T^3 process. In addition to controlling maximum retort temperature, the use of steam has the following advantages:

1. The steam increases the combustion rate of residual carbon in spent shale through the water gas shift reactions.

2. The steam increases the hydrogen production per ton to oil shale by reacting with the carbon monoxide. The steam increases the reaction rate of residual carbon with carbon dioxide by increasing the porosity of spent shale. The residual carbon in the spent shale reacts with the carbon dioxide to produce carbon monoxide which reacts with the steam to produce hydrogen.

3. The steam reduces the oil loss due to thermal cracking in the retorting zone by increasing CO_2 production rate in the combustion zone. The steam minimizes the oil loss when it is released from the raw shale surface.

4. The steam increases the retorting rate compared with the recycle gas.

3.6.2 Solid Wastes

According to the Magic Circle proposed alternative process for their operation in Utah for 35,000 bbl/day plant, about 49,000 tons per stream day of spent shale would require disposal. It would be carried to the disposal area from the processing plant on a covered belt conveyor. Because of the continuous flow of spent shale from the processing plant, the conveyor and associated equipment are scheduled to operate continuously. There is no other information available for solid waste streams composition.

3.6.3 Characteristics of Solid Wastes

There is no information on the characteristics of solid wastes in the Magic Circle proposal utilizing T^3 technology.

3.7 HYTORT OIL SHALE RETORTING

3.7.1 Retorting Operation

Controlled heating of oil shale in hydrogen at elevated pressures can be used to produce synthetic natural gas (SNG) or a synthetic crude oil [DRI, SAI & KSC; 68-03-2795]. The relative amounts of these products can be varied by proper selection of the operating conditions. Oil shale research at the Institute of Gas Technology (IGT) began in the 1950s, sponsored by the American Gas Association and later by the Gas Research Institute, and this program led to the development of the HYTORT process. It has been tested in a process development unit (PDU) which is a one-tonne per hour adiabatic reactor and is claimed to increase shale organic carbon conversions relative to other processes.

The design of the PDU is shown in Figure 3.7-1. Oil shale, crushed to 0.5 inches average size, with the fines removed, is fed through screw mechanisms to two adiabatic reactors, the first for shale prehydrogenation and the second for shale gasification. The pressures used have been from 200-500 psi and average temperatures from 1200 - 1475°F. For Colorado shales the oil-to-gas ratio in the products changes from 4:1 to about 0.5:1 as the average temperature increases from 1200°F to 1475°F. The rate of addition of shale and the rate of temperature rise also influence the ratio of products. HYTORT shale oils from both eastern and western shales have relatively low viscosities and pour points. They can be pumped through pipelines in the raw state, in contrast to most shale oils from thermal retorting processes. HYTORT shale oil from Colorado shale is lighter in color and contains 30 percent less sulfur than oils from conventional retorting, because of the high pressure hydrogen treatment. However, like all shale oils, HYTORT oil requires catalytic hydrotreating to reduce its sulfur and nitrogen to acceptable levels.

The conceptual design of a zoned reactor for the HYTORT process is shown in Figure 3.7-2. Crushed shale (fines removed) is fed to the high pressure reactor through liquid sealed lockhoppers. The shale moves downward countercurrent to the hydrogen-rich gas flow through the reactor. A small amount of oxygen is injected into the reactor near its center for heat balance purposes. Processed shale is removed from the reactor through liquid sealed lockhoppers. Product gas is scrubbed to recover water and shale oil. A bleed stream of the clean gas is sent to the steam reformer where hydrocarbons are converted into hydrogen. All the make up hydrogen requirements of hydroretorting and catalytic hydrotreating are to be produced in this fashion and it is expected that no hydrogen will need to be purchased. In some trials by the HYTORT process, 2,500 to 4,000 scf of hydrogen is chemically consumed per ton of Devonian shale. The shale oil is catalytically hydrotreated to produce a low sulfur, low nitrogen refinery feedstock product and a plant utility fuel stream.

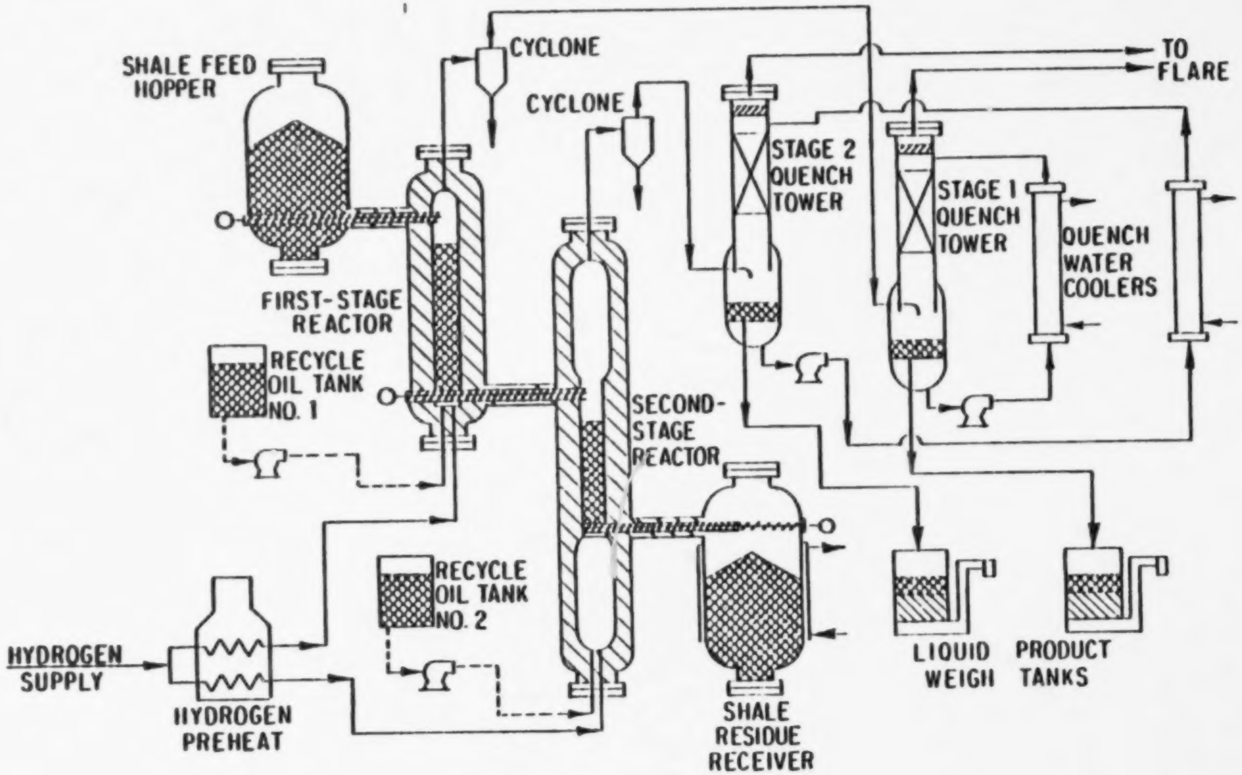

SHALE FEED HOPPER
CYCLONE
CYCLONE
TO FLARE
STAGE 2 QUENCH TOWER
STAGE 1 QUENCH TOWER
QUENCH WATER COOLERS
FIRST-STAGE REACTOR
RECYCLE OIL TANK NO. 1
SECOND-STAGE REACTOR
RECYCLE OIL TANK NO. 2
HYDROGEN SUPPLY
HYDROGEN PREHEAT
SHALE RESIDUE RECEIVER
LIQUID WEIGH
PRODUCT TANKS

Figure 3.7-1. Diagram of IGT Oil Shale Gasification Process Development Unit.
Source: DRI, SAI & KSC; 68-03-2795

3.7.2 Solid Wastes

There is no information on the subject of solid wastes or waste streams of the HYTORT process.

3.7.3 Characteristics of Solid Wastes

Leaching characteristics and hydraulic properties of retorted oil shales have been investigated by McWhorter [EPA-600/D-84-228, 1984]. The data are presented in Tables 3.7-1 to 3.7-3.

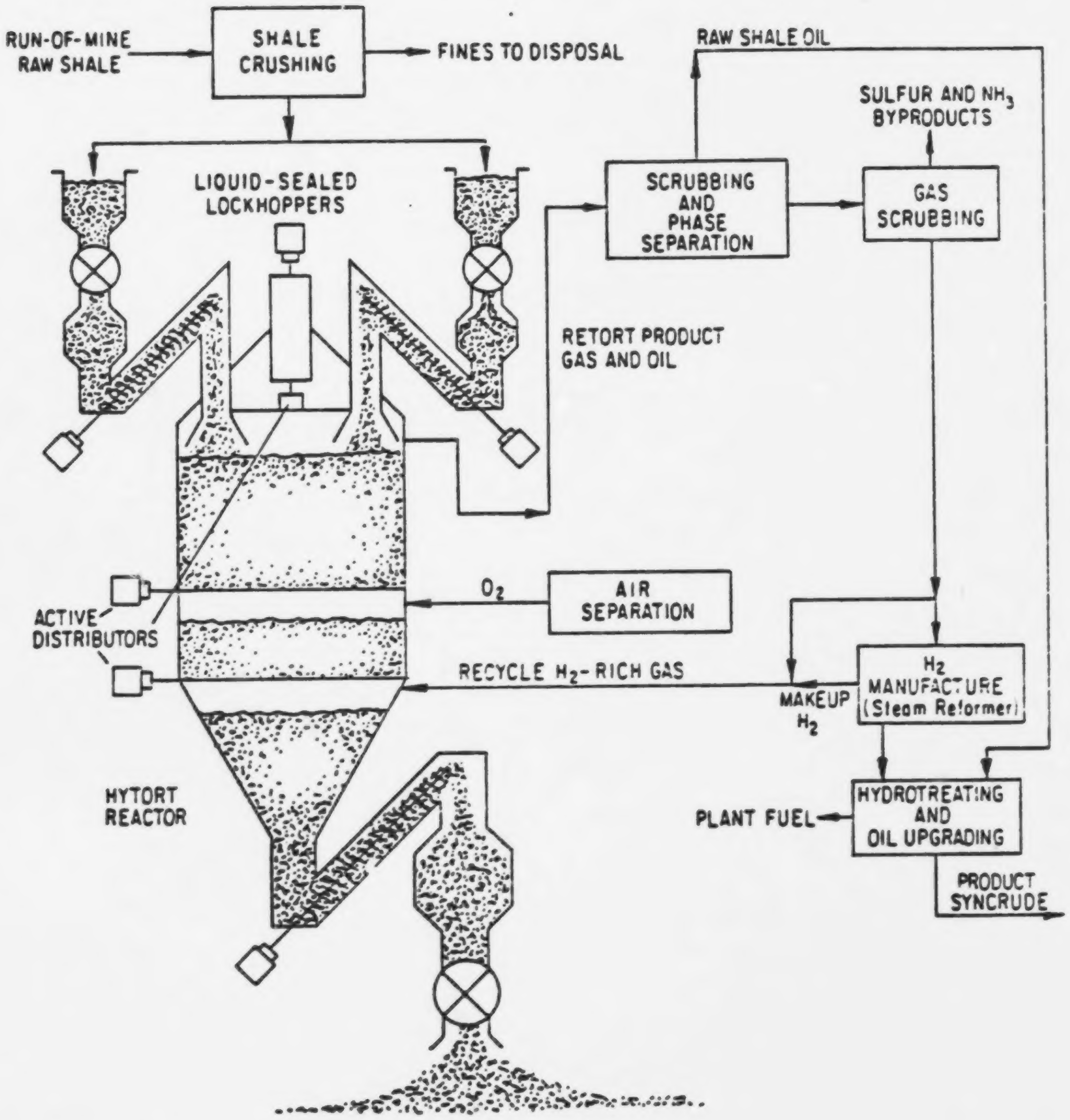

RUN-OF-MINE
RAW SHALE
SHALE
CRUSHING
FINES TO DISPOSAL
RAW SHALE OIL
SULFUR AND NH_3
BYPRODUCTS
LIQUID-SEALED
LOCKHOPPERS
SCRUBBING
AND
PHASE
SEPARATION
GAS
SCRUBBING
RETORT PRODUCT
GAS AND OIL
O_2
AIR
SEPARATION
ACTIVE
DISTRIBUTORS
RECYCLE H_2-RICH GAS
H_2
MANUFACTURE
(Steam Reformer)
MAKEUP
H_2
HYTORT
REACTOR
PLANT FUEL
HYDROTREATING
AND
OIL UPGRADING
PRODUCT
SYNCRUDE

Figure 3.7-2. HYTORT Commercial Plant Conceptual Design.
Source: DRI, SAI & KSC; 68-03-2795

TABLE 3.7-1. WATER HOLDING CAPACITY OF HYTORT PROCESSED SHALES AT VARIOUS PRESSURES AND BULK DENSITIES[a]

Sample	Pressure 14.7 psi (1 bar)	44.1 psi (3 bar)	73.5 psi (5 bar)	147 psi (10 bar)	200 psi (13.6 bar)
Packed to a BD=1.30 g/cc	35.2	33.7	32.6	31.8	31.0
BD=1.45 g/cc	31.0	27.6	25.3	23.8	23.2
BD=1.60 g/cc	30.5	30.3	28.9	25.4	24.6

BD = Bulk density

[a] Table entries are moisture contents (w) expressed on a weight % basis (weight of water per unit weight of dry solids).

Source: EPA-600/D-84-228, 1984

TABLE 3.7-2. CONCENTRATIONS IN ASTM WATER SHAKE AND RCRA TESTS EXTRACTS - HYTORT SPENT SHALES

Parameter	Units	ASTM	RCRA
pH	-	9.76	
EC	µmhos/cm @ 25°	1160	4.94
ALK	mg/L	205	1540
H_2CO_3	mg/L	0.08	430
HCO_3	mg/L	166	13278
CO_3	mg/L	41.1	525
TDS	mg/L	1060	0.002
F	mg/L	3.4	1740
Cl	mg/L	12.4	8.95
PO_4	mg/L	0.59	<0.1
NO_3	mg/L	5.2	2.3
SO_4	mg/L	178	97
Zn	mg/L	0.212	0.477
Fe	mg/L	0.033	0.078
Co	mg/L	<0.005	0.120
Li	mg/L	0.005	0.019
V	mg/L	<0.002	<0.002
NH_3	mg/L	16.4	1.66
B	mg/L	1.110	0.340
Cd	mg/L	<0.001	0.013
Be	mg/L	<0.0005	<0.0005
Mg	mg/L	0.23	85
P	mg/L	0.33	0.4
Si	mg/L	21	3.7
Mo	mg/L	1.92	<0.05
Mn	mg/L	0.015	8.98
Ni	mg/L	<0.005	0.971
Na	mg/L	26	11
Cu	mg/L	0.013	0.023
Al	mg/L	0.86	0.44
Ca	mg/L	250	319
Ba	mg/L	0.120	0.210
K	mg/L	60	22
Cr	mg/L	0.030	<0.005
Sr	mg/L	0.85	1.0
Pb	mg/L	<0.01	<0.01
Ag	mg/L	<0.001	0.003
TL	mg/L	<0.005	<0.005
Se	mg/L	<0.020	<0.02
As	mg/L	0.037	0.010
Hg	mg/L	<0.001	<0.001

Source: EPA-600/D-84-228, 1984

TABLE 3.7-3. LEACHABLE MASS FROM HYTORT SHALE AS INDICATED BY THE ASTM PROPOSED WATER SHAKE TEST AND RCRA EXTRACTION TEST - mg/g

Parameter	ASTM	RCRA
Na	0.104	0.220
Ca	1.00	6.380
Mg	0.001	1.700
SO_4	0.712	1.940
Cl	0.050	0.179
F	0.014	-
B	0.004	0.007
Mo	0.008	0.006
Al	0.003	0.044
TDS	4.24	34.80

Source: EPA-600/D-84-228, 1984

3.8 GEOKINETICS HORIZONTAL *IN SITU* OIL SHALE RETORTING

3.8.1 Retorting Operation

In the Geokinetics, Inc (GKI) horizontal *in situ* retorting process, known as LOFRECO (low front end cost)(U.S. Patent 4037657), a specific pattern of blast holes is drilled from the cleared surface through any overburden and into the oil shale bed. The schematics of the process is shown in Figure 3.8-1. Explosives are placed in these holes and detonated by use of a carefully timed and planned blast system. The blast yields a well-fragmented mass of shale with high permeability, and also produces a slightly sloping (approximately 4°) bottom surface that allows the produced oil to drain into a sump for collection. The fragmented zone constitutes the *in situ* retort. The void space in the fragmented zone comes from lifting the overburden, produces small uplift of the surface. Submerged-type oil well pumps are used to lift the recovered oil to surface storage tanks.

Burning charcoal is introduced into drilled holes at the upper end of the rubblized zone to ignite the retort. Air inlet piping is also installed at this end of the retort. The burn front, consisting of a vertical wall approximately 30-ft high, travels toward the deep or low end of the retort. The objective is to retort the shale from one end to the other in a plug-flow fashion by maintaining a burn front that occupies the entire cross section of the bed. Typically the front travels at a speed of one foot per day.

3.8.2 Solid Wastes

Since this is an *in situ* process very little above ground solid waste is expected to be generated. The largest volume of solid waste is the retorted shale which is left below ground.

3.8.3 Characteristics of Solid Wastes

The chemical composition of leachates is summarized in Table 3.8-1 [Fox, 1983]. Recent data are presented in Tables 3.8-2 and 3.8-3; and in Figure 3.8-2 [DOE/FE/60177-1590, April 1984].

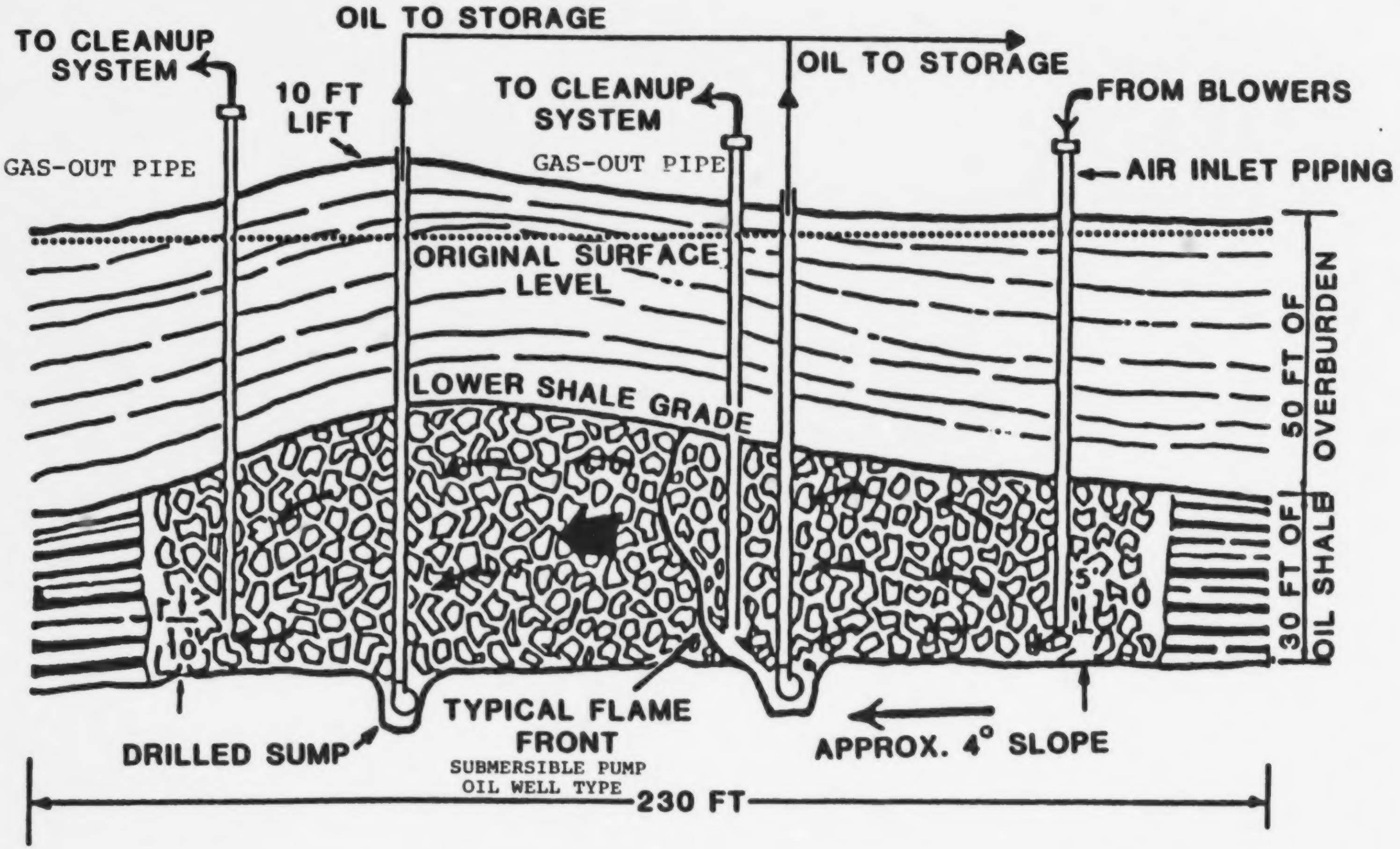

OIL TO STORAGE
TO CLEANUP SYSTEM
10 FT LIFT
TO CLEANUP SYSTEM
OIL TO STORAGE
FROM BLOWERS
GAS-OUT PIPE
GAS-OUT PIPE
AIR INLET PIPING
ORIGINAL SURFACE LEVEL
LOWER SHALE GRADE
50 FT OF OVERBURDEN
30 FT OF OIL SHALE
1
10
5
1
DRILLED SUMP
TYPICAL FLAME FRONT
SUBMERSIBLE PUMP
OIL WELL TYPE
APPROX. 4° SLOPE
230 FT

Figure 3.8-1. Geokinetics Horizontal *In Situ* Retort.

TABLE 3.8-1. INORGANIC COMPOSITION OF LEACHATES FROM GEOKINETICS SPENT SHALE (mg/L)

	Cleave et al., 1979	Krause et al., 1980	Krause, et al., 1980
As	-	0.01 - 0.2	0.03 - 0.3
B	-	0.5 - 6.7	0.6 - 2.6
Ca	747	-	-
Cl	29	-	-
EC, µmhos/cm	-	321 - 16,200	741 - 8,430
F	-	0.32 - 10.1	2.3 - 13
HCO_3	797	-	-
K	34.4	-	-
Mg	0.2	-	-
Mo	-	0.4 - 17.1	0.7 - 6.4
Na	542	-	-
Se	-	<0.001 - 1.3	0.006 - 0.16
SO_4	2,298	170 - 16,435	790 - 5,595
pH	-	8.8 - 11.6	9.2 - 11.6
Type of study	shaker	Column	Ball mill/batch
Particle diameter	-	-1 in.	-10 mesh
Solid-to-liquid ratio, g/mL	0.5	-	0.4
Contact time	48 hr	1 hr	2 wk
Other	-	3 x 50 cm glass column	-

Source: Fox, July 1983

TABLE 3.8-2. MAJOR ION COMPOSITION OF LEACHATE (GEOKINETICS SPENT SHALE)

$\frac{vt}{L}$	pH	EC µmhos/cm	Alk P/P $CaCO_3$	Ca P/P	P P/P	K P/P	Na P/P	Cl P/P	F P/P	HCO_3 P/P	CO_3 P/P	SO_4 P/P
0.010	12.27	80380	1289	282	-	-	14350	284	10.0	9.68	768.8	44360
0.021	12.23	78960	1204	225	0.18	22900	13700	275	7.2	9.93	717.8	43460
0.036	12.15	73190	1104	281	-	-	13100	306	13.5	10.85	657.1	42880
0.052	12.15	73190	1104	283	-	-	12150	263	11.3	10.66	637.8	40580
0.071	12.11	67990	1008	192	-	-	11350	197	4.2	10.81	599.5	37530
0.090	12.11	62330	960	288	0.12	12900	10350	179	6.8	10.46	570.5	35710
0.108	12.09	61660	926	293	-	-	9650	164	4.7	10.56	550.4	34040
0.136	12.08	58060	868	286	-	-	9050	163	4.9	10.06	516.1	32450
0.163	12.06	54330	840	325	-	-	8700	159	4.9	10.14	498.8	31230
0.191	12.04	50950	794	248	-	-	8300	142	6.9	10.05	471.5	29340
0.217	11.99	49750	760	282	-	-	7750	131	5.6	10.78	450.5	27730
0.244	12.00	45330	732	280	-	-	6340	131	14.7	10.21	434.4	25730
0.268	12.01	46120	743	274	-	-	6240	127	3.0	10.17	440.8	26410
0.293	12.02	42950	700	313	-	-	5260	112	4.3	9.28	415.4	24000
0.311	12.02	41230	694	285	-	-	5200	114	3.0	9.22	412.1	23500
0.349	11.99	39250	664	353	-	-	5000	109	3.9	9.43	394.0	21910
0.381	11.98	37210	636	289	-	-	4700	106	7.6	9.17	377.1	18340
0.396	12.00	35560	680	275	-	-	4280	99	6.6	9.37	403.4	17710
0.496	12.00	32280	624	364	-	-	4100	89	7.2	8.69	370.0	16100
0.510	11.97	28810	569	264	0.09	6680	3520	80	5.5	8.51	337.5	14740
0.630	11.96	26420	555	340	-	-	2960	73	5.5	8.52	329.1	13400
0.641	11.89	23790	500	286	-	-	2460	66	4.7	8.86	295.5	12270
0.684	11.91	22190	489	310	-	-	2600	61	4.7	8.24	289.1	11260
0.737	11.87	20380	448	355	-	-	2340	63	6.9	8.34	264.5	8490
0.885	11.91	18340	458	434	-	-	1900	55	5.8	7.76	271.0	7950
0.896	11.89	16520	430	362	-	-	1660	47	5.4	7.75	254.4	7150
0.917	11.86	15770	416	308	-	-	1620	48	5.8	8.00	245.5	7170
1.123	11.86	14040	400	340	-	-	1160	40	5.0	7.60	236.5	6520
1.135	11.81	13460	390	290	-	-	1000	34	4.7	8.25	229.8	5800
1.147	11.83	11730	372	351	-	-	940	30	3.6	7.61	219.5	5320
1.269	11.79	10550	360	294	-	-	1050	28	2.4	7.97	212.1	5430
1.528	11.79	9700	346	397	-	-	914	24	1.7	7.78	203.8	4830
1.540	11.75	8660	320	329	-	-	753	21	4.9	7.12	188.3	3780
1.647	11.76	7950	319	381	-	-	653	20	4.5	7.67	187.4	3610
1.766	11.73	7350	300	312	-	-	560	23	3.1	7.74	176.2	3380
1.977	11.72	6900	294	362	0.05	798	486	15	3.2	7.70	172.9	3230
1.985	11.68	6410	280	442	-	-	420	15	3.4	8.02	164.1	3050

Source: DOE/FE/60177-1590, April 1984

Key

Average permeability = $\bar{K} = 4.6 \times 10^{-4}$ cm/s

$\frac{vt}{L}$ = pore volume

TABLE 3.8-3. CONCENTRATION (mg/L) OF TRACE ELEMENTS FOR SELECTED PORE VOLUMES OF LEACHATE (GEOKINETICS SPENT SHALE)

	$\frac{vt}{L}$			
	0.021	0.090	0.510	1.977
P	0.4	0.3	0.2	0.1
Al	0.6	0.4	0.5	0.3
Fe	0.04	0.02	0.01	<0.01
Mn	0.03	0.01	0.01	<0.01
Cu	0.18	0.15	0.14	<0.01
Zn	0.03	0.02	0.06	<0.01
Ni	0.03	0.01	0.01	<0.01
Mo	33.1	17.4	6.0	0.7
Cd	0.01	0.01	0.01	<0.01
Cr	0.07	0.03	0.01	<0.01
Sr	2.3	13.4	15.4	13.5
B	11.9	7.7	6.1	2.6
Ba	0.19	0.21	0.14	0.09
Pb	0.1	<0.1	<0.1	<0.1
As	<0.1	<0.1	<0.1	<0.1
Se	2.4	1.1	0.4	<0.1

Source: DOE/FE/60177-1590, April 1984

Key

$K = 4.6 \times 10^{-4}$ cm/s

$\frac{vt}{L}$ = pore volume

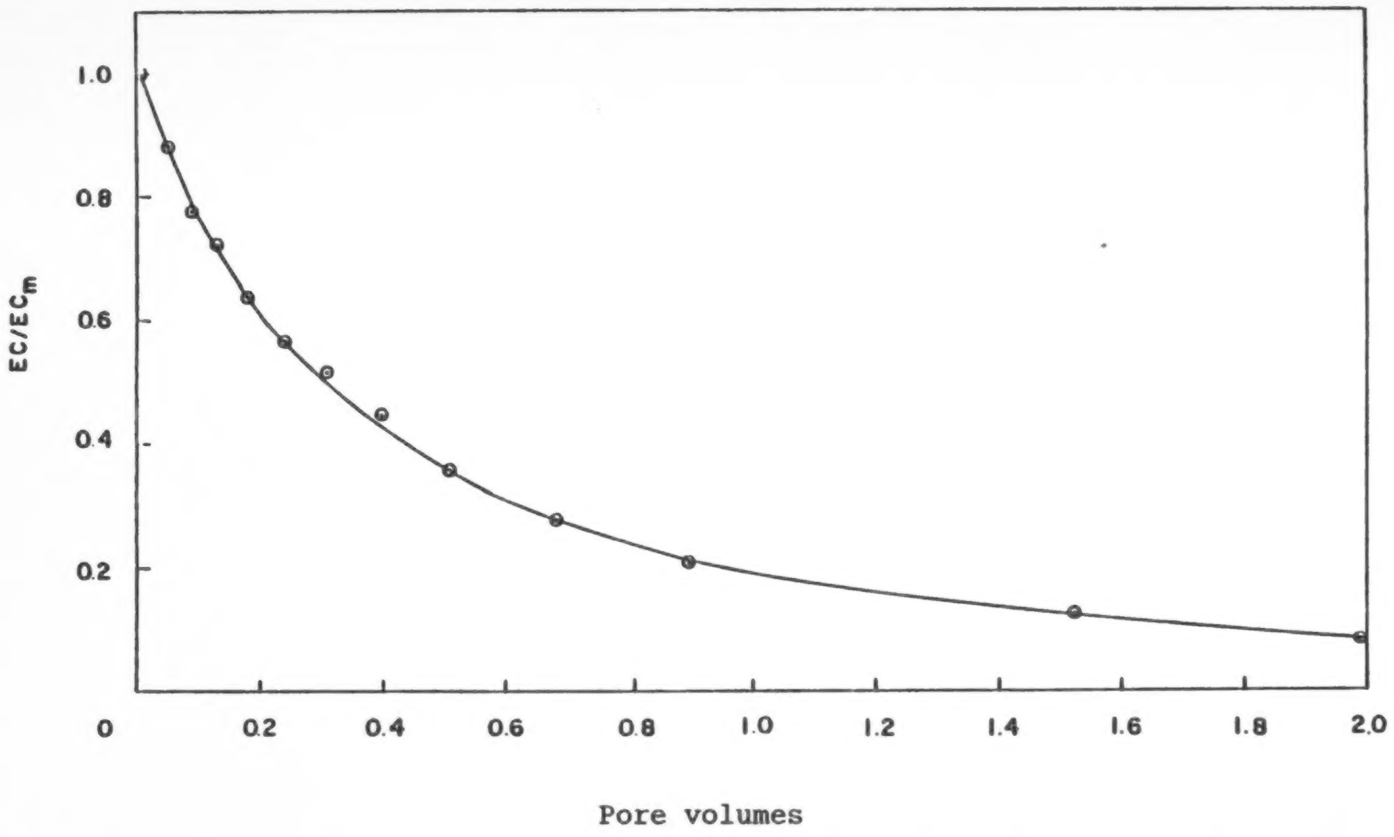


Figure 3.8-2. Electrical Conductivity Breakthrough Curve for Leachate from Geokinetics Spent Shale

Source: DOE/FE/60177-1590, April 1984

3.9 SUPERIOR CIRCULAR GRATE OIL SHALE RETORTING

3.9.1 Retorting Operation

A commercial-sized Superior retort incorporates a circular traveling grate retort about 200 ft in diameter, covered by a hood and made gas-tight by water seals at the sides (Figure 3.9-1). The doughnut-shaped retort is divided into five separately enclosed sections: a loading zone, a retorting zone, a residual carbon recovery zone, a cooling zone, and finally an unloading zone.

The raw shale is fed to the traveling grate retort so that the finest material is at the bottom and coarsest on top. The prepared bed of shale passes first into the retorting zone where it contacts a stream of hot gases, and retorting occurs as the hot gases pass down through the bed of shale. The oil and gas mixture passes to a separator/condenser system where shale oil is recovered, and the cooled recycle gases then pass through the retorted shale bed in the cooling zone of the retort to cool the processed shale before dumping, and heat the recycle gas.

The retorted shale travels from the retorting zone to the carbon recovery zone where evolution of shale oil vapors is completed, and residual carbon is burned in a mixture of recycle gas and preheated combustion air. From the combustion zone, the processed shale travels to the shale cooling zone where recycle gas is heated by the hot shale. The shale is cooled further by ambient air. See Figure 3.9-2 for schematics of directly heated operation of the Superior retort. Processed shale is discharged through mechanical seals or a water seal which wets the shale for dust control. The traveling grate is sealed between stationary hoods on top of the bed and the windboxes underneath by water troughs on both sides, which allows for expansion and contraction of the retort structural members.

Preheated recycle gas from the shale cooling zone is heated further by mixing with hot combustion gases and the mixture is sent to the shale heating zone to complete the cycle.

Retort product gas is taken as a side stream from the recycle gas. A high Btu (400-600 Btu/scf) gas is produced in the indirect-heated mode. Gas from the direct-heated mode is low-Btu (80-130 Btu/scf).

3.9.2 Solid Wastes

Figure 3.9-3 presents the process operations and projected waste streams for the Superior Circular Grate Process. Dust fines are generated in the raw shale mining and crushing phase and are disposed of in the solid waste pile. Retorted shale is moistened prior to the discharge from the circular grate.

3.9.3 Characteristics of Solid Wastes

No data are available on the characteristics of the retorted shale and other solid wastes. The soluble materials extracted by water in Superior spent shale has been reported as 142 lb/ton (TRW, May 1977).

Table 3.9-1 presents process water quality parameters. Tables 3.9-2 and 3.9.3 show results of leachate tests. It is not known if the shale used in these tests had undergone moisturization or leaching for alumina and soda ash removal. The information in Table 3.9-4 and 3.9-5 summarizes Superior leachate data using distilled water and process water on process shale.

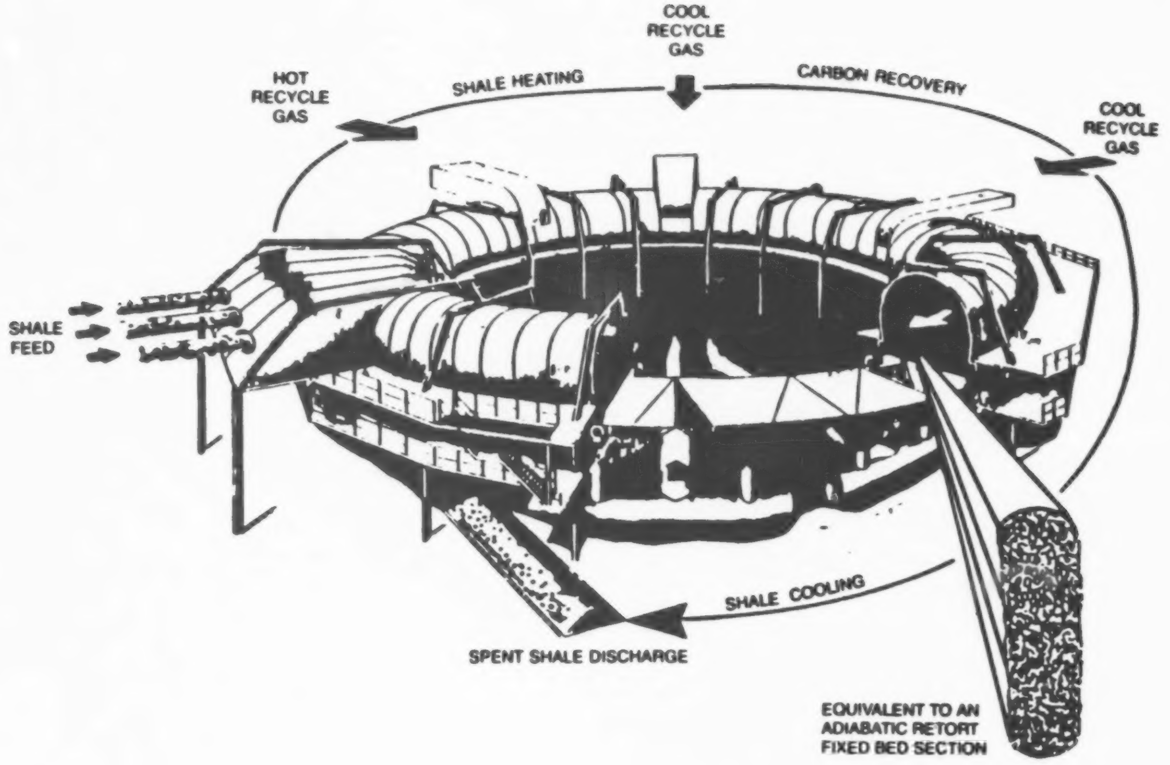
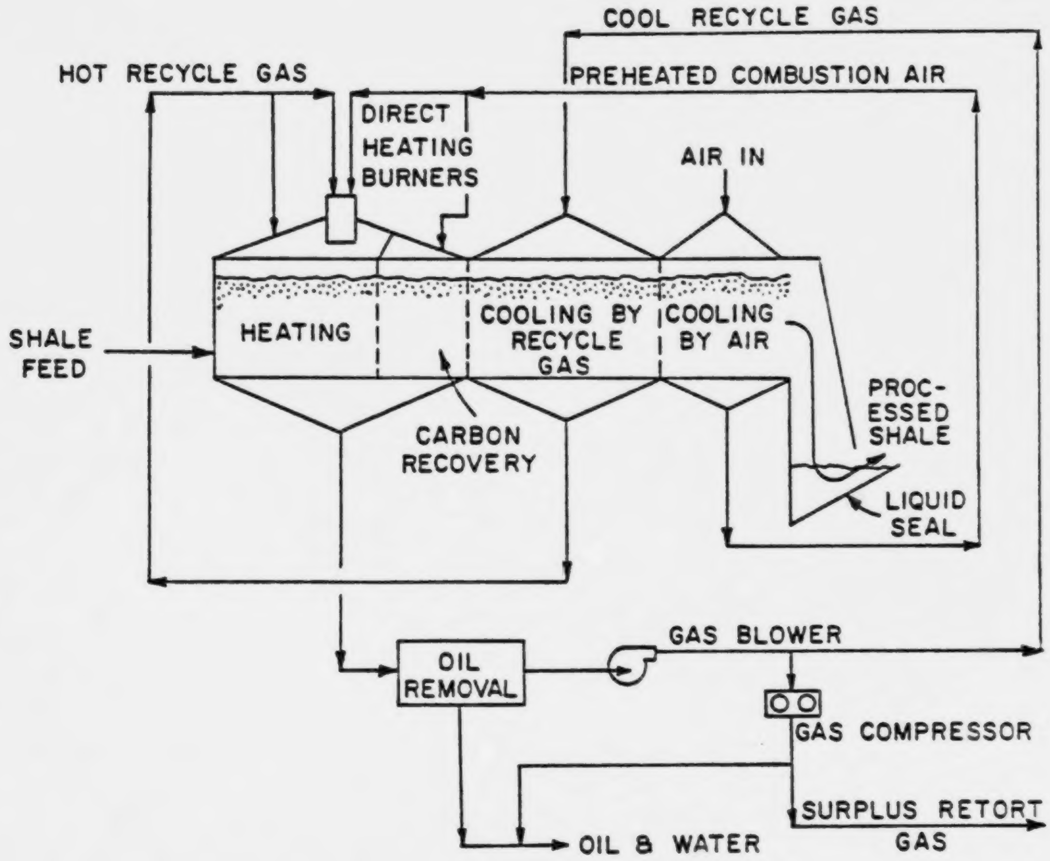

COOL
RECYCLE
GAS
HOT
RECYCLE
GAS
SHALE HEATING
CARBON RECOVERY
COOL
RECYCLE
GAS
SHALE
FEED
SHALE COOLING
SPENT SHALE DISCHARGE
EQUIVALENT TO AN
ADIABATIC RETORT
FIXED BED SECTION

Figure 3.9-1. Superior retorting process retort showing movement of charge through various zones.

Source: BLM, February 1983


COOL RECYCLE GAS
HOT RECYCLE GAS
PREHEATED COMBUSTION AIR
DIRECT HEATING BURNERS
AIR IN
SHALE FEED
HEATING
COOLING BY RECYCLE GAS
COOLING BY AIR
PROCESSED SHALE
CARBON RECOVERY
LIQUID SEAL
GAS BLOWER
OIL REMOVAL
GAS COMPRESSOR
SURPLUS RETORT GAS
OIL & WATER

NOTE:
THE CIRCULAR PATH OF THE SOLIDS BED IS PICTURED AS A STRAIGHT PATH FOR CLARITY

Figure 3.9-2. Superior direct-heated process.
Source: DRI, SAI & KSC; 68-03-2795

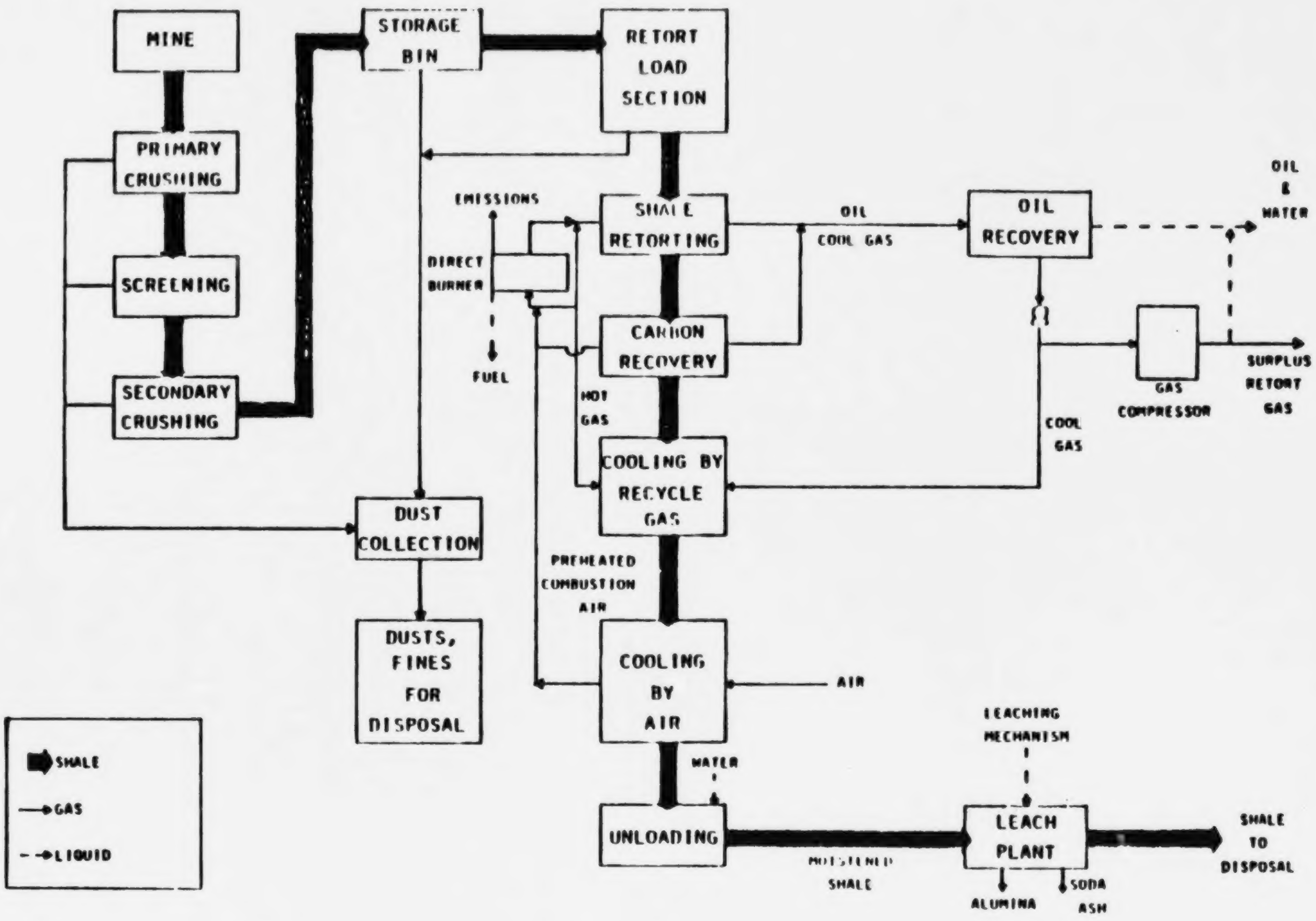

MINE
PRIMARY CRUSHING
SCREENING
SECONDARY CRUSHING
STORAGE BIN
RETORT LOAD SECTION
SHALE RETORTING
CARBON RECOVERY
COOLING BY RECYCLE GAS
COOLING BY AIR
UNLOADING
DUST COLLECTION
DUSTS, FINES FOR DISPOSAL
EMISSIONS
DIRECT BURNER
FUEL
HOT GAS
PREHEATED COMBUSTION AIR
AIR
WATER
OIL
COOL GAS
OIL RECOVERY
OIL & WATER
GAS COMPRESSOR
SURPLUS RETORT GAS
COOL GAS
LEACHING MECHANISM
LEACH PLANT
MOISTENED SHALE
ALUMINA
SODA ASH
SHALE TO DISPOSAL
SHALE
GAS
LIQUID

Figure 3.9-3. Superior process flow diagram and major waste streams.
Source: Monsanto, 1984

TABLE 3.9-1. GENERAL WATER QUALITY PARAMETERS OF SUPERIOR OIL SHALE PROCESS WATER

Parameter	
pH	7.0
Conductivity, μmhos/cm	>8,500
Ammonia nitrogen[a]	1,600
TOC[a]	5,000
Cl^-[a]	350
$SO_4^=$[a]	3,000
Arsenic[a], 5[b]	0.25
Barium[a], 100[b]	<0.1
Boron[a]	1.83
Cadmium[a], 1[b]	<0.1
Chromium[a], 5[b]	<0.1
Lead[a], 5[b]	<0.1
Lithium[a]	0.18
Manganese[a]	1.23
Molybdenum[a]	<0.1
Nickel[a]	<0.1
Selenium[a], 1[b]	<0.1
Silver[a], 5[b]	0.24
Strontium[a]	0.21
Thorium[a]	<0.1

[a] All values in mg/L.

[b] RCRA hazardous waste classification threshold value for element concentration in leaches in mg/L

Source: Jackson & Jackson, 1982

TABLE 3.9-2. INORGANIC COMPOSITION OF SUPERIOR LEACHATE PRODUCED BY THE ASTM TEST METHOD D3987

Element	Concentration[a] mg/L
Ag	<0.1
As	<0.1
B	0.6 - 0.22
Ba	<0.1
Cd	<0.1
Cl	<5
Cr	<0.1
EC (μmho/cm)	2400 - 3250
Li	0.51 - 0.80
Mn	<0.1
Mo	0.39 - 0.46
NH_3	0 - 2
Ni	<0.1
Pb	<0.1
Se	0.14 - 0.20
SO	896 - 1908
Sr	0.33 - 0.58
Th	0.43 - 0.56
TOC	<20
pH	9.4

[a] Samples were prewetted to 20 wt % with distilled water, compacted, equilibrated for 0 to 4 weeks, fractured, and leached by ASTM D3987. In this test, 350 g of solid are leached in 1.4 liters of distilled water and the leachate diluted to 2 liters prior to analysis. Chemical analysis was by inductively coupled argon plasma spectrometry and other methods.

Source: Fox, July 1983

TABLE 3.9-3. THE EFFECT OF COPRODUCTED RETORT WATERS ON THE QUALITY OF SUPERIOR LEACHATES FROM SPENT SHALES[a]

	Moisturization water composition	Leachate composition[b]	
		Spent shale moisturized	
	Retort water	Distilled water	Retort water
As	0.25	<0.1	0.14
B	1.83	0.16	0.29
Ba	<0.1	<0.1	<0.1
Cl	350	>5	18
Cr	<0.1	<0.1	<0.1
EC, μmhos/cm	>8,500	3,250	3,900
Li	0.18	0.51	0.63
Mn	1.23	<0.1	<0.1
Mo	<0.1	0.39	0.38
Ni	<0.1	<0.1	<0.1
Se	<0.1	0.14	0.15
SO_4	3,000	896	1,073
Sr	0.21	0.33	0.39
TOC	5,000	>20	53
pH	7.0	9.4	9.2

[a] All values in ppm except EC which is in μmho/cm.

[b] Samples produced by leaching fractured cores cured for 4 weeks using ASTM D3987 (350 g of spent shale are batch leached in 1,400 mL distilled water; the final leachate was diluted to 2,000 mL prior to analysis). Spent shale cores were produced by moisturizing each sample (12.5% water (w/w)) and compacting it according to ASTM D698-78.

Source: Fox, July 1983

TABLE 3.9-4. EFFECT OF DISTILLED WATER, AND TIME ON THE LEACHATE QUALITY OF MOISTENED, COMPACTED SUPERIOR SPENT SHALES

Shale core age	Water quality parameters					
	pH	Conductivity µmhos/cm	Cl^-, mg/L	$SO_4^=$, mg/L	NH_3-N, mg/L	TOC, mg/L
0 Week	9.4	2400	>5	1908	0	>20
4 Week	9.4	3250	>5	896	2	>20

Source: Jackson & Jackson, 1982

3.10 UNION OIL A OIL SHALE RETORTING

3.10.1 Retorting Operation

All three of the processes developed by Union Oil are variations of an upflow vertical kiln retort using a rock-pump shale feeding mechanism [EPA-600/2-80-205a, 1980]. The retorts are known as Retort A, Retort B, and SGR-3. In all three processes, the oil shale is pushed upward through the retort while the gas flow is downward. In Retort A, the heat for pyrolysis is generated by the internal combustion of residual carbon on the spent shale. In Retort B and the SGR retort, the heat is supplied indirectly by externally heated hot gases.

The Retort A process was developed through 2-, 50-, and 1,000-ton/day pilot plants that were operated before 1960. A view of the Retort A process is shown in Figure 3.10-1. The retort is an inverted cone fitted with a rock-pump shale feeder that pushes the oil shale upward through the vessel. Air is injected at the top of the retort to support combustion of the residual carbon on the retorted shale fragments in the upper portion of the retort. This combustion provides the heat necessary to retort the upward-flowing shale.

The crushed shale feed is removed from the hopper and transferred to the bottom of the retort by a shale feeder. As the shale enters the retort, it is contacted by a countercurrent flow of hot product gases leaving the combustion and retorting zones above. In this lower zone, the gas-cooling zone, heat is transferred from the hot gases to the cool incoming shale. The feed is preheated, and the oil vapors are condensed while the gases are cooled. Passing up through the retort, the preheated shale enters the retorting or pyrolysis zone. The gases passing downward in this area, having just left the combustion zone, heat the shale to a temperature such that organic material is pyrolyzed, producing shale oil vapor, product gas, and residual carbon on the surface of the shale. As the gaseous products of pyrolysis are evolved, they are swept downward by the flow of combustion gases.

The retorted shale fragments then enter the combustion zone where they encounter preheated combustion air passing down through the retort. This air sustains the combustion of the residual carbon that remains on the surface of the shale after retorting. Temperatures in this zone may reach 2000°F, high enough to fuse a portion of the shale. In earlier versions of the retort, retorting spiral plows were used to break clinkers and remove retorted shale. In later versions, these plows were not used.

TABLE 3.9-5. CONCENTRATION OF METALS IN LEACHATES FROM SUPERIOR RETORTED SHALES:

Element shale	ASTM 0[a]	ASTM 4[a]	RCRA 0[a]	RCRA 4[a]
Arsenic	<0.1	<0.1	0.13	0.1
Barium	<0.1	<0.1	0.84	0.63
Boron	0.22	0.16	0.96	0.71
Cadmium	Less than 0.1 mg/l for all cases			
Chromium	<0.1	<0.1	0.10	<0.1
Lead	0.1	<0.1	0.16	0.32
Lithium	0.80	0.51	0.36	0.49
Manganese	<0.1	<0.1	3.3	3.8
Molybdenum	0.46	0.39	0.25	0.22
Nickel	<0.1	<0.1	0.19	0.18
Selenium	0.20	0.14	0.45	0.48
Silver	Less than 0.1 mg/L for all cases			
Strontium	0.58	0.33	10.5	10.0
Thorium	0.56	0.43	1.4	1.4

[a] Shale age in weeks after moistening with distilled water.

Source: Jackson and Jackson, 1982

3.10.2 Solid Wastes

There is not much information available on the amounts of solid wastes or solid waste streams of the Union Oil A process.

3.10.3 Characteristics of Solid Wastes

Pertinent data are presented in Tables 3.10-1 to 3.10-4.

TABLE 3.10-1. PHYSICAL PROPERTIES OF UNION A SPENT SHALE

	Shale ash 16 years old Composite sample in-place
Particle size	
Percent cobble (1" - 6")	8 - 28
gravel (4.76 mm - 1")	43 - 57
sand (0.074 - 4.76 mm)	15 - 23
silt (0.005 - 0.074 mm)	} 8 - 13
clay (-0.005 mm)	
Texture	Graded gravel to silty gravel
Color	Light brown
Solids density, g/cc	2.36
Dry bulk density, pcf	60.3 - 90.5
Field moisture, wt. %	12.1 - 45.0

Source: TRW/DRI, May 1977.

TABLE 3.10-2. CHEMICAL PROPERTIES OF UNION A RETORTED SHALE

Components[a],	Retort A shale ash, wt. %
SiO_2	35.3
CaO	27.2
MgO	9.0
Al_2O_3	8.5
Fe_2O	7.3
Na_2O	5.5
K_2O	2.8
SO_3	0.1
P_2O_5	2.2
Mineral CO_2	1.6
Organic C	0.5
Ignition loss @ 950°C	2.1
Free silica (quartz)	<2.0
pH of slurry	12.5 - 13 (est.)

[a] Analyses determined by heating sample to 950°C except for pH measurement. Analyses by Union Research Department.

Source: Wildung and Zachara, 1980

TABLE 3.10-3. ANALYSIS OF LEACHATE OBTAINED IN LABORATORY TESTS OF UNION A RAW AND RETORTED SHALE

	Quantity extracted per unit weight of shale (kg/tonne)	
	Raw shale	Retorted Shale
Inorganics		
K^+	0.24	6.25
Na^+	0.48	21.0
Ca^{++}	0.1	3.27
Mg^{++}	0.01	0.91
HCO_3^-	0.75	0.28
Cl^-	0.22	0.33
$SO_4^=$	0.79	62.3
Total		
kg/tonne	2.59	94.3
lbs/ton	5.18	188

Source: TRW/DRI, May 1977.

TABLE 3.10-4. INORGANIC COMPOSITION OF LEACHATES FROM UNION A SPENT SHALE,

Components	mg/L
Ca	327
Cl	33
CO_3	21
F	3.4
HCO_3	28
K	625
Mg	91
Na	2,100
SO_4	6,230
TDS	10,011
EC, µmhos/cm	11,050
pH	9.94
Particle diameter	-40 mesh
Solid-to-liquid ratio, g/mL	0.1
Contact time, min	5

Source: Fox, 1983

3.11 UNION OIL B OIL SHALE RETORTING

3.11.1 Retorting Operation

In the Retort B process, shown in Figure 3.11-1, crushed oil shale in the 1/8 to 2 in. size range flows through two feed chutes to the solids pump. The solids pump consists of two piston and cylinder assemblies which alternately feed shale to the retort. As shale is moved upward through the retort by the upstroke of the piston, it is met by a stream of 950 to 1,000°F recycle gas from the recycle gas heater flowing downward. The rising oil shale bed is heated to retorting temperature by countercurrent contact with the hot recycle gas, resulting in the evolution of shale oil vapor and make gas. This mixture of shale oil vapor and make gas is forced downward by the recycle gas, and cooled by contact with the cold incoming shale in the lower section of the retort cone. In the disengaging section surrounding the lower cone, the liquid level is controlled by withdrawing the oil product, and the recycle and make gas are removed from the space above the liquid level.

The make gas is first sent to a venturi scrubber for cooling and heavy ends removal by oil scrubbing. A portion of the 800 Btu/SCF make gas is then processed by compression and oil scrubbing to remove additional heavy ends, followed by a Stretford unit to remove hydrogen sulfide. The sweetened make gas is used as plant fuel. The remaining gas, taken off after the venturi scrubber, is recycled to the retort through the recycle gas heater to provide the heat for oil retorting.

The rundown oil from the retort is treated sequentially for solids, arsenic, and lightends removal. The solids removal is accomplished by two stages of water washing. The shale fines are collected in the water phase which is recycled to the water seal. The water seal is a Union Oil concept, in which a water level is maintained in the conveyor for retorted shale removal to seal the retort pressure from atmosphere. For arsenic removal, a proprietary Union Oil process employing an adsorbent is utilized to reduce the arsenic content of the raw shale oil from 50 ppm to 2 ppm. The dearsenated shale oil is sent to a stripping column for stabilization and stripping prior to shipment. This partially upgraded shale oil can now be marketed as a low sulfur burner fuel in various locations in the United States, and is also a suitable feedstock for refineries that have adequate hydrotreating capacity. The crude shale oil from the Retort B process has a specific gravity of 0.918 (22.7°API), a pour point of 60°F, and a kinematic viscosity of 20 centistokes (98.2 SUS) at 100°F. It typically contains 1.74 weight percent nitrogen and 0.81 weight percent sulfur.

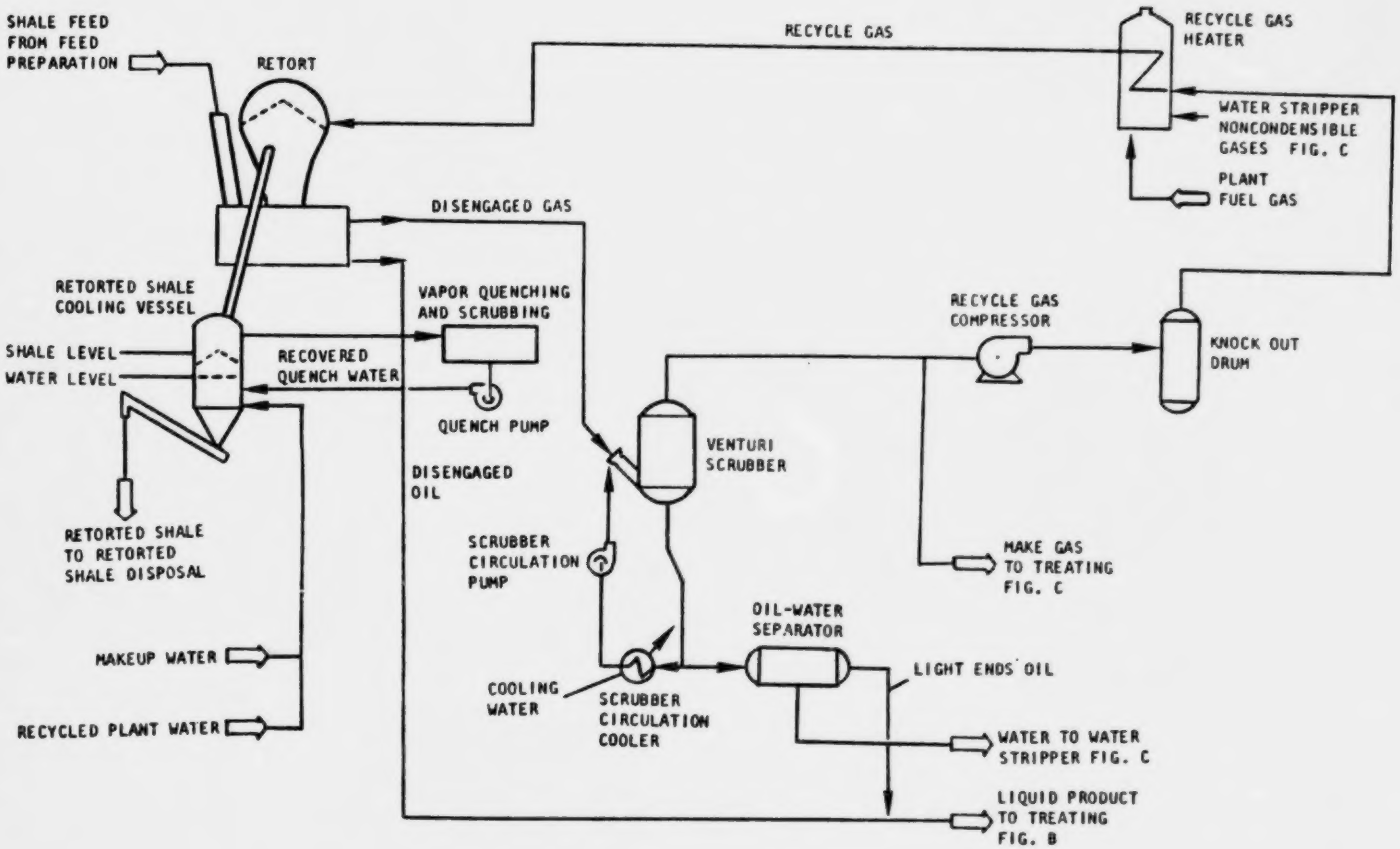

SHALE FEED FROM FEED PREPARATION
RETORT
RECYCLE GAS
RECYCLE GAS HEATER
WATER STRIPPER NONCONDENSIBLE GASES FIG. C
PLANT FUEL GAS
DISENGAGED GAS
RETORTED SHALE COOLING VESSEL
VAPOR QUENCHING AND SCRUBBING
RECYCLE GAS COMPRESSOR
KNOCK OUT DRUM
SHALE LEVEL
WATER LEVEL
RECOVERED QUENCH WATER
QUENCH PUMP
VENTURI SCRUBBER
DISENGAGED OIL
RETORTED SHALE TO RETORTED SHALE DISPOSAL
SCRUBBER CIRCULATION PUMP
MAKE GAS TO TREATING FIG. C
OIL-WATER SEPARATOR
MAKEUP WATER
COOLING WATER
SCRUBBER CIRCULATION COOLER
LIGHT ENDS OIL
RECYCLED PLANT WATER
WATER TO WATER STRIPPER FIG. C
LIQUID PRODUCT TO TREATING FIG. B

Figure 3.11-1. Flow Diagram for Retort System in Union Oil Retort B Prototype Plant.
Source: TRW, March 1977.

3.11.2 Solid Wastes

Figure 3.11-2 presents the process operations and waste streams for the Union B prototype plant. The solid waste streams are highlighted in the figure. Dusts and fines are generated from the primary crushing, screening, and storage of raw shale prior to the retorting phase. Retorted shale is cooled and moistened for disposal.

Table 3.11-1 lists an inventory of the solid waste streams, the percent each stream represents of the total mass requiring disposal, and the components of each waste stream.

3.11.3 Characteristics of Solid Wastes

Tables 3.11-2 through 3.11-3 provide chemical and physical properties of retorted shale. Table 3.11-4 shows results of analysis of the process water to be used to moisturize the spent shale. Table 3.11-5 list leachate data. Table 3.11-6 shows results of RCRA testing conducted on Union B shale.

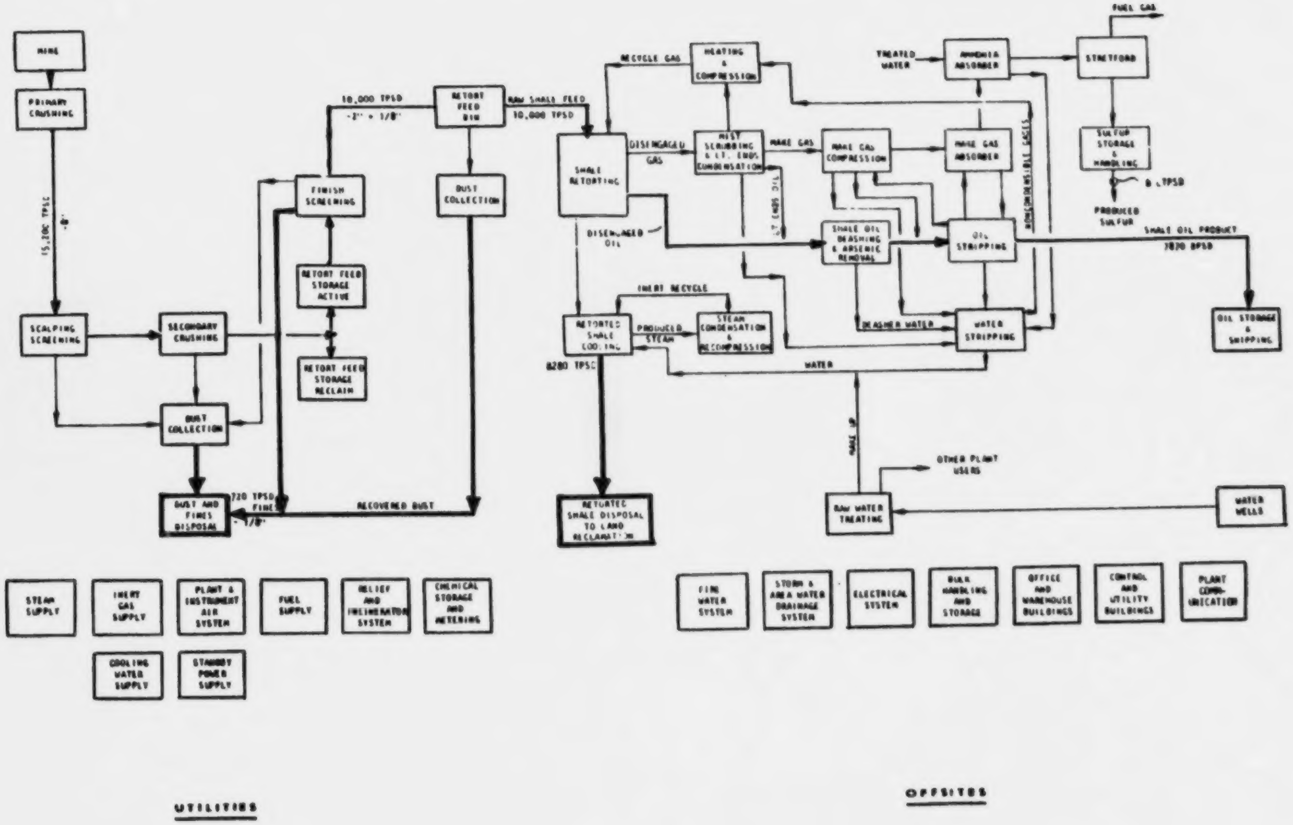

MINE
PRIMARY CRUSHING
15,200 TPSD
-8"
SCALPING SCREENING
SECONDARY CRUSHING
DUST COLLECTION
DUST AND FINES DISPOSAL
720 TPSD FINES
- 1/8"
FINISH SCREENING
RETORT FEED STORAGE ACTIVE
RETORT FEED STORAGE RECLAIM
10,000 TPSD
-2" + 1/8"
RETORT FEED BIN
DUST COLLECTION
RECOVERED DUST
RAW SHALE FEED
10,000 TPSD
SHALE RETORTING
RECYCLE GAS
HEATING & COMPRESSION
DISENGAGED GAS
MIST SCRUBBING & LT. ENDS CONDENSATION
LT ENDS OIL
MAKE GAS
MAKE GAS COMPRESSION
DISENGAGED OIL
SHALE OIL DEASHING & ARSENIC REMOVAL
TREATED WATER
AMMONIA ABSORBER
MAKE GAS ABSORBER
OIL STRIPPING
NONCONDENSIBLE GASES
STRETFORD
FUEL GAS
SULFUR STORAGE & HANDLING
8 LTPSD
PRODUCED SULFUR
SHALE OIL PRODUCT
7820 BPSD
OIL STORAGE & SHIPPING
INERT RECYCLE
RETORTED SHALE COOLING
PRODUCED STEAM
STEAM CONDENSATION & RECOMPRESSION
DEASHER WATER
WATER STRIPPING
8280 TPSD
WATER
MAKE UP
RETORTED SHALE DISPOSAL TO LAND RECLAMATION
RAW WATER TREATING
OTHER PLANT USERS
WATER WELLS
STEAM SUPPLY
INERT GAS SUPPLY
PLANT & INSTRUMENT AIR SYSTEM
FUEL SUPPLY
RELIEF AND INCINERATOR SYSTEM
CHEMICAL STORAGE AND METERING
COOLING WATER SUPPLY
STANDBY POWER SUPPLY
UTILITIES
FIRE WATER SYSTEM
STORM & AREA WATER DRAINAGE SYSTEM
ELECTRICAL SYSTEM
BULK HANDLING AND STORAGE
OFFICE AND WAREHOUSE BUILDINGS
CONTROL AND UTILITY BUILDINGS
PLANT COMMUNICATION
OFFSITES

Figure 3.11-2. Block Flow Diagram for Union Oil Retort B Prototype Plant [TRW, March 1977]

TABLE 3.11-1. INVENTORY OF STREAMS TO BE DISPOSED OF AS SOLID WASTES IN UNION B PROCESS

Description of stream	Amount generated for 50,000 bpd plant, t/d	Percent of total solid waste	Component of concern	Remarks
Raw shale dust	4,000	5.7		
Moisturized retorted shale	65,850	94.0	Salts	20% moisture content
Spent catalyst (upgrading)	0.14	0	Nickel, cobalt, molybdate	Containerized and land filled
Spent adsorbents	0.87	0.001	Arsenic	40 wt % arsenic
Absorption solution filter cakes	0.21	0.00003		Amine unit DEA filter drain, containerized & land filled off-site
Waste treatment sludges	137.0	0.20		Lime sludges
Spent zeolites	0.01	0		From boiler feedwater treatment
Spent catalyst (hydrogen plant)	0.44	0.00007	Variety	Off-site disposal
Claus unit catalyst	0.06	0	Spent bauxite	
Wellman-Lord sulfur recovery unit purge solid	0.43	0.00007	70 wt % Na_2SO_4, 20 wt %Na_2SO_3, 11 wt % $Na_2S_2O_3$, and less than 1% H_2O	

Source: Monsanto, August 1984. Based on TRW, March 1977

TABLE 3.11-2. PHYSICAL PROPERTIES OF UNION B SPENT SHALE[a]

	Initial	After compaction at 12.375 ft. lbs/cf
Particle size		
Percent cobble (1" - 6")	-	-
gravel (4.76 mm - 1")	74	37
sand (0.074 - 4.76 mm)	16	39
silt (0.005 - 0.074 mm)	9	17
clay (-0.005 mm)	1	7
Texture	Silty gravel	
Color	Black	
Solids density, g/cc	2.59	
Dry bulk density, g/cc	0.98	1.45
Field moisture, wt. %	16	21-23

[a] Analyses by Woodward-Clyde Consultants.

Source: TRW, May 1977.

TABLE 3.11-3. CHEMICAL PROPERTIES OF UNION B RETORTED SHALE

Components[a],	wt %
SiO_2	31.5
CaO	19.6
MgO	5.7
Al_2O_3	6.9
Fe_2O_3	2.8
Na_2O	2.2
K_2O	1.6
SO_3	1.9
P_2O_5	0.4
Mineral CO_2	22.9
Organic C	4.3
Nitrogen, Kjeldahl	0.2
Ignition loss @ 950°C	26.9
Free silica (quartz)	8.0
pH of slurry	8.7

[a] Analyses determined by heating sample to 950°C except for pH measurement. Analyses by Union Research Department.

Source: Battelle PNL 3830

TABLE 3.11-4. ESTIMATED[a] COMPOSITION OF UNION B PROCESS WATER IN THE ACTIVE BASIN AND THE REUSE WATER SUMP

Parameter	Active Basin (mg/l)	Reuse Water Sump (mg/l)
Alkalinity (as $CaCO_3$	5,800	2,000
Carbonate (as CO_3)	2,500	400
Bicarbonate (as HCO_3)	1,000	1,700
Chemical Oxygen Demand	200	5,500
Total Organic Carbon	50	1,350
Total Dissolved Solids	4,500	2,600
Total Solids	4,500	3,100
Hardness (as $CaCO_3$)	1,100	900
Ammonia	2	35
Sulfides (as H_2S)	0	100
Phenols	10	125
Cyanide (CN)	-	20
Oil & Grease	50	1,300
Sulfate	3,000	500
Sodium	1,500	1,500
Arsenic	0	6.5
Chromium	5	0.5
pH units	8-10	8-10

[a] These values are maximum design case estimates based on preliminary bench-scale tests and engineering calculations.

Source: Union Oil, January 1984

TABLE 3.11-5. INORGANIC COMPOSITION OF LEACHATES FROM UNION B SPENT SHALE, mg/L

	Union, 1979c	Cleave et al., 1979
Ag	<0.02	<0.0009
Al	0.2	-
As	0.004	0.001
B	0.68	0.97
Ba	0.07	0.078
Be	<0.01	-
Ca	95	243
Cd	<0.01	0.016
Cl	<2	7.0
CN	<0.01	-
Co	<0.1	-
CO_3	0	-
Cr	<0.005	<0.011
Cu	0.02	<0.011
EC, µmhos/cm	750	-
F	6.1	-
Fe	<0.05	<0.025
HCO_3	25	172
Hg	0.0005	-
K	2.5	7.4
Li	0.09	-
Mg	24	58
Mn	0.02	<0.007
Mo	0.4	-
Na	130	109
Ni	<0.04	-
N, Kjeldahl	0.6	-
NH_3-N	<1.0	-
NO_3	<10	-
NO_2	<5	-
Oil and grease	6	-
Pb	<0.05	0.009
Phenols	<1	-
PO_4	<10	-
$S^{=}$	<0.01	-
Se	<0.005	<0.001
SO_4	570	878
Sr	1.2	-
TDS	800	1,518
TOC	<1	11.3
V	<0.03	-
Zn	0.02	0.025
pH	7.7	8.33
Particle diameter	-	-
Solid-to-liquid ratio, g/mL	0.1	0.1
Contact time, min	5	30

Source: Fox, 1983.

TABLE 3.11-6. RCRA TESTING OF SIMULATED UNION B OIL SHALE PLANT WASTES

	UNISULF sulfur	Moistened Retorted shale plus fines[a]	Maximum allowed	Minimum allowed
Ignitiability				
Causes fire through friction	No	No	-	-
Oxidation	0°F	0°F	-	-
Corrosivity				
a) pH	-	-	12.5	2.0
b) steel corrosion (in./yr)	-	-	0.25	-
Reactivity				
Yield gases, vapors or flames when exposed to water	No	No		
Yields H_2S or HCN when exposed to pH 2 buffer	No	No		
Reacts Explosively				
(a) when subjected to burner flame	No	No		
(b) when under heated confinement	No	No		
EP Toxicity, mg/l				
Arsenic	<0.01	0.07	5.0	
Barium	0.2	<2.7	100.0	
Cadmium	<0.01	<0.01	1.0	
Lead	<0.05	<0.05	5.0	
Mercury	0.002	<0.0005	0.2	
Selenium	<0.0005	<0.0005	1.0	
Silver	<0.02	<0.02	5.0	

[a] Moistened with simulated process water.

Source: Union Oil, January 1984

3.12 UNION OIL SGR OIL SHALE RETORTING

3.12.1 Retorting Operation

In early 1977, Union Oil announced a process, that, when retrofitted to a Retort B prototype unit, would further improve the economics of the process by utilizing the residual carbon left on the spent shale. This process, known as Steam-Gas Recirculation (SGR-3), [DRI, SAI & KSC; 68-03-2795; EPA-600/2-80-205a, 1980], provides for the combustion of the residual carbon in a separate vessel, thus producing enough hot flue gas to supply all of the retort heat requirements. This two-vessel SGR-3 process produces a high BTU (980-BTU/scf) product gas from the retort vessel while maintaining a high thermal efficiency (83 percent) by using the residual carbon on the spent shale in the combustor vessel. Following the removal of C_4 plus hydrocarbons and acid gases from the gas stream, the heating value is reduced to approximately 800 BTU/scf. This value can be increased to more than 1,000 BTU/scf by methanation. A flow diagram for the process is shown in Figure 3.12-1.

Because of the design of the rock pump feed mechanism, all of the proposed Union Oil processes utilize fairly large shale fragments of 2 to 1/8 inches. As in the other vertical kiln type processes, very little attrition occurs during the retorting process, and thus the spent shale fragments leave the retort essentially the same size as they entered. The spent shale from the direct-heated Union retorts would be gray in color, having had some of the residual carbon burned off. The indirect-heated retorts, on the other hand, would discharge shale still containing the residual carbon. The SGR-3 process employs a separate spent shale combustor unit. The spent shale from these processes, therefore, would be light-colored, containing very little residual carbon.

The composition of the product gas from the retort largely depends on the mode of heating. Indirectly heated retorts like the SGR will produce a high-BTU gas product whereas the product from direct-heated retorts will have a low BTU content because of nitrogen dilution.

3.12.2 Solid Wastes

Nothing is available on this subject.

3.12.3 Characteristics of Solid Wastes

Pertinent data are presented in Tables 3.12-1 to 3.12-10.

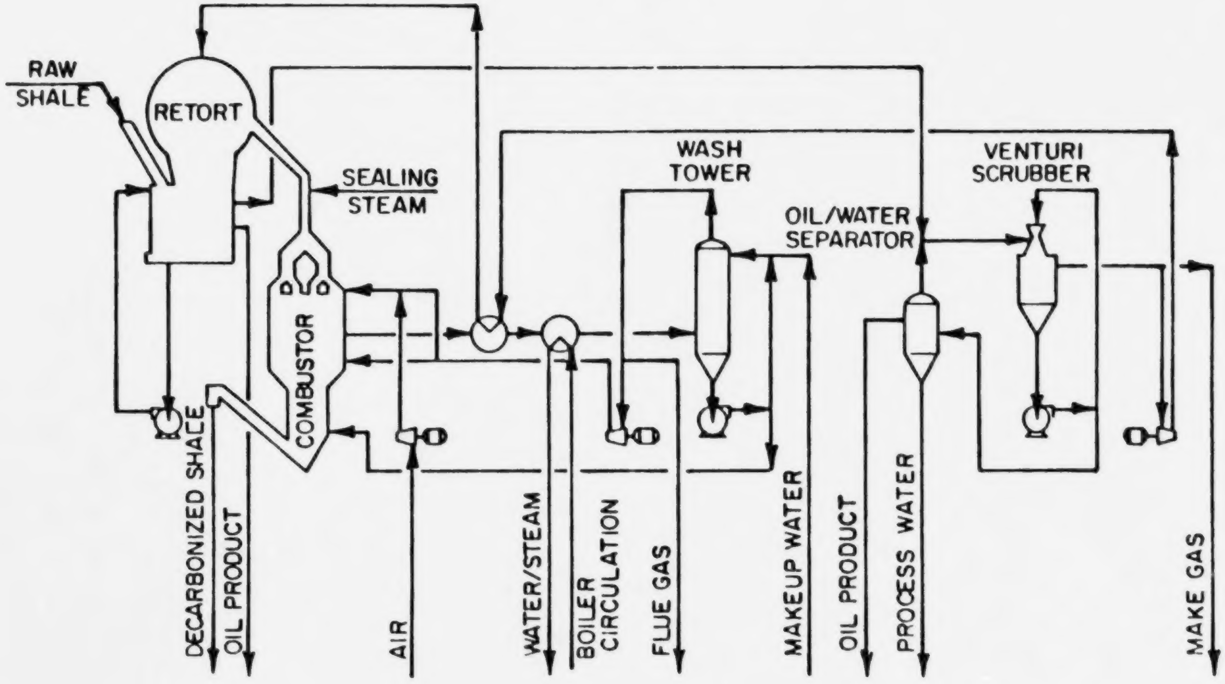

RAW SHALE
RETORT
SEALING STEAM
COMBUSTOR
WASH TOWER
OIL/WATER SEPARATOR
VENTURI SCRUBBER
DECARBONIZED SHALE
OIL PRODUCT
AIR
WATER/STEAM
BOILER CIRCULATION
FLUE GAS
MAKEUP WATER
OIL PRODUCT
PROCESS WATER
MAKE GAS

Figure 3.12-1. Diagram of Union Oil SGR-3 Retorting Process.
Source: EPA-600/2-80-205a, 1980

TABLE 3.12-1. PHYSICAL PROPERTIES OF UNION SGR SPENT SHALE[a]

	Decarbonized Shale Fresh	
	Initial	After Compaction at 12.375 ft.lbs/cf
Particle Size:		
% Cobble (1" - 6")	-	-
% Gravel (4.76 mm - 1")	75	53
% Sand (0.074 - 4.76 mm)	16	14
% Silt (0.005 - 0.074 mm)	5	33
% Clay (-0.005 mm)	4	
Texture	Silty Gravel	
Color	Buff	
Solids Density, g/cc	2.69	
Dry Bulk Density, pcf	-	68.5

[a] Analyses by Woodward-Clyde Consultants

Source: TRW, May 1977.

TABLE 3.12-2. PARTICLE SIZE, pH, AND ELECTRICAL CONDUCTIVITY OF SPENT OIL SHALES PRODUCED BY UNION SGR RETORTING PROCESS

Process	Particles Size >2mm	Particles Size <2mm	pH[a]	Electrical Conductivity[a] (μmhos/cm)
Union decarbonized	87	13	11.4	3

[a] Electrical conductivity and pH were determined on a saturated paste extract prepared from spent shale particles less than 2mm in size.

Source: Schuman et al., 1976.

TABLE 3.12-3. CHEMICAL PROPERTIES OF UNION SGR RETORTED SHALE

Components[a]	
SiO_2	39.2
CaO	27.3
MgO	8.2
Al_2O_3	8.9
Fe_2O_3	3.8
Na_2O	3.7
K_2O	2.7
SO_3	1.4
P_2O_5	0.5
Mineral CO_2	3.1
Organic C	0.3
Nitrogen, Kjeldahl	-
Ignition loss @ 950°C	3.4
Free Silica, quartz	2.5
pH of slurry	12.5

[a] Analyses determined by heating sample to 950°C except for pH measurement. Analyses by Union Research Department. All numbers except that for pH are in weight percent.

Source: Wildung & Zachara, 1980

TABLE 3.12-4. AMOUNTS AND QUALITY OF SURFACE RUNOFF FROM UNION SGR DECARBONIZED SHALE LYSIMETER STUDY

	Shale						
	1975 Spring	1975 Irrigation	1976 Spring	1976 Summer	1977 Spring	1977 Summer	1978 Spring
Total runoff, cm	0.6	0.2	1.5+[a]	0.1	1.5	0.1	1.1
Electrical Conductivity, µmhos/cm	224+	880	290	260	604	215	230
Salinity Hazard	Low	High	Medium	Medium	Medium	Low	Low
Sodium Adsorption Ratio	0.1	2.2	0.4	0.2	0.4	0.9	0.3
Sodium Hazard	Low	Low	Low	Low	Low	Low	Low
Sediment Yield, kg/ha	-	-	29	33	35	24	10

	15 cm Soil Cover Over Shale						
	1975 Spring	1975 Irrigation	1976 Spring	1976 Summer	1977 Spring	1977 Summer	1978 Spring
Total runnoff, cm	1.4+	0.8	6.5+[a]	0.7	3.5	1.6	7.3
Electrical Conductivity, µmhos/cm	62[b]	663	100	248	120	160	43
Salinity Hazard	Low	Medium	Low	Low	Low	Low	Low
Sodium Adsorption Ratio	0.1	0.1	0.4	0.2	0.3	0.2	0.1
Sodium Hazard	Low	Low	Low	Low	Low	Low	Low
Sediment Yield, kg/ha	-	-	3	1,684	1	1,240	134

[a] The collectors on these treatments were found to leak in 1976, thus this value is low.

[b] Estimated from total dissolved solids.

Source: Herron et al, 1980

TABLE 3.12-5. WATER QUALITY OF PERCOLATE FROM UNION SGR DECARBONIZED SHALE LYSIMETERS

	1975 Irrigation	1976 Spring	1976 Summer	1977 Spring	1977 Summer	1978 Spring
Total Percolate, cm	0.6	3.7+	0.1	0.1	0.1	7.3
Electrical Conductivity, μmhos/cm	7,352	9,400	7,770	3,573	3,700	10,000
Salinity Hazard	Very High	Very High	Very High	Very High	Very High	Very High
Sodium Adsorption Ratio	72.5	99.5	74.1	58.5	60.2	115.6
Sodium Hazard	High	High	High	High	High	High
pH	9.1	12.1	9.5	9.5	10.6	11.8

Source: Herron et al., 1980

TABLE 3.12-6. ANALYSIS OF SPRING SNOWMELT RUNOFF AND PERCOLATE FROM UNION SGR DECARBONIZED SHALE LYSIMETER STUDY. APRIL 21,1976

	Runoff samples		Percolate samples	
Lysimeter number	4	5	4	5
Total runoff on percolate (liters/plot)	143.8	132.5	280.1+	382.3+
EC µmhos/cm @ 25°C	260	320	8,000	10,800
pH	7.7	7.9	12.0	12.2
Suspended solids, ppm	8.0	2.6	14.7	11.3
Dissolved solids, ppm	152.0	174.0	3,382	3,922
Settleable solids, ml/L	0.1	0.1	0.1	0.1
Na, ppm	10.0	11.0	1,050	1,480
Ca, ppm	13.7	16.3	19.3	8.6
Mg, ppm	15.7	19.5	2.7	0.0
K, ppm	3.6	4.2	170.0	210.0
Cl, ppm	17.5	7.5	37.5	65.0
SO_4, ppm	44.0	61.0	271.0	625.0
CO_3, ppm	0	0	1,154.0	1,065.0
HCO_3, ppm	77.6	77.4	236.0	487.0
PO_4, ppm	0.7	0.8	1.6	0.6
NO_3, ppm	0.5	7.9	2.5	11.4
As, ppm	0.005	0.005	0.35	0.31
SAR	0.43	0.43	60.4	138.6

Source: Herron, et al, 1980

TABLE 3.12-7. ANALYSIS OF RUNOFF AND PERCOLATE SAMPLES COLLECTED AUGUST 5, 1976 FROM UNION SGR DECARBONIZED SHALE LYSIMETER STUDY

	Runoff samples		Percolate samples	
Lysimeter number	4	5	4	5
Total runoff on percolate (liters/plot)	3.5	0	0	8.0
EC µmhos/cm @ 25°C	260	-[a]	7,700	460
pH	7.2	-[a]	-[b]	9.5
Suspended solids, ppm	1,452.0	-[a]	-[b]	190.0
Dissolved solids, ppm	216.0	-[a]	-[b]	6,628.0
Settleable solids, ml/L	13.0	-[a]	-[b]	5.5
Na, ppm	0.21	-[a]	-[b]	85.2
Ca, ppm	1.79	-[a]	-[b]	2.64
Mg, ppm	0.87	-[a]	-[b]	0
K, ppm	3.3	-[a]	-[b]	470.0
Cl, ppm	7.5	-[a]	-[b]	5.0
SO_4, ppm	25.6	-[a]	-[b]	835.0
CO_3, ppm	0	-[a]	-[b]	782.0
HCO_3, ppm	109.0	-[a]	-[b]	3,489.0
NO_3, ppm	3.2	-[a]	-[b]	7.2
PO_4, ppm	1.2	-[a]	-[b]	1.9
As, ppm	0.001	-[a]	-[b]	0.49
SAR	0.18	-[a]	-[b]	74.1

[a] No runoff.

[b] No percolate.

Source: Herron, et al, 1980

TABLE 3.12-8. ANALYSIS OF SPRING SNOWMELT RUNOFF AND PERCOLATE FROM UNION SGR DECARBONIZED SHALE LYSIMETER STUDY. MARCH 30, 1977

Lysimeter number	Runoff samples 4	 5	Percolate samples 4	 5
Total runoff on percolate (liters/plot)	132.5	143.8	6.1	17.8
EC µmhos/cm @ 25°C	530	3,500[a]	3,150	4,000
pH	6.75	6.9	9.05	10.0
Suspended solids, ppm	2.25	4.75	67.33	40.88
Dissolved solids, ppm	346	496	2,454	2,792
Settleable solids, ml/L	<0.1	<0.1	1.6	0.4
Na, ppm	19.4	11.8	910	875
Ca, ppm	29.12	48.25	19.13	8.3
Mg, ppm	28.52	66	3.0	3.0
K, ppm	17.6	10.1	258	274
Cl, ppm	10.0	10	5.0	24
SO_4, ppm	190	294	663	1,080
CO_3, ppm	0.0	0.0	90.6	266
HCO_3, ppm	81.2	91.03	1,690	1,329
PO_4, ppm	0.54	0.34	1.78	1.0
NO_3, ppm	8.62	17.51	22.18	10.41
As, ppm	<0.001	<0.001	0.16	0.14
SAR	0.62	0.26	50.9	66.1

[a] This reading is felt to be in error. Using a regression of EC verses dissolved solids, this reading should be approximately 678 µmhos/cm.

Source: Herron, et al, 1980

TABLE 3.12-9. ANALYSIS OF RUNOFF AND PERCOLATE SAMPLES COLLECTED AUGUST 30, 1977 FROM UNION SGR DECARBONIZED SHALE LYSIMETER STUDY

	Runoff samples		Percolate samples	
Lysimeter number	4	5	4	5
Total runoff on percolate (liters/plot)	4.5	0	0	11.3
EC µmhos/cm @ 25°C	215			3,700
pH	7.0			10.6
Suspended solids, ppm	2,080			50.8
Dissolved solids, ppm	158			5,878
Settleable solids, ml/L	6.3			0.2
Na, ppm	4.8			1,870
Ca, ppm	16.41			3.12
Mg, ppm	6.21			45.52
K, ppm	6.0			590
Cl, ppm	5.0			17.5
SO_4, ppm	10.9			1,090
CO_3, ppm	0.0			1,006
HCO_3, ppm	98.45			4,329
PO_4, ppm	6.56			1.99
NO_3, ppm	1.32			37.84
As, ppm	<0.001			0.122
SAR	0.87			60.2

Source: Herron, et al, 1980

TABLE 3.12-10. ANALYSIS OF SPRING SNOWMELT, RUNOFF, AND PERCOLATE FROM UNION SGR DECARBONIZED SHALE LYSIMETER STUDY. MAY 3, 1978

	Runoff samples		Percolate samples	
Lysimeter number	4	5	4	5
Total runoff on percolate (liters/plot)	46.0	155.2	10.0	3.6
EC µmhos/cm @ 25°C	230	230	7,100	12,900
pH	7.4	8.5	11.5	12.5
Suspended solids, ppm	9.4	3.10	4,798	5,032
Dissolved solids, ppm	124	140	754.9	549.2
Settleable solids, ml/L	0.1	<0.1	<0.1	<0.1
Na, ppm	4.95	7.9	1,200	1,430
Ca, ppm	15.3	23.37	25.5	3.4
Mg, ppm	15.3	14.62	8.1	0.90
K, ppm	33.8	3.9	380	510
Cl, ppm	33.6	2.8	8.8	29.4
SO_4, ppm	47.8	90.5	1,870	1,662
CO_3, ppm	0.0	5.97	212	985
HCO_3, ppm	84.27	62.6	1,083	1,083
PO_4, ppm	0.21	0.20	0.81	0.84
NO_3, ppm	0.14	1.37	3.72	4.10
As, ppm	0.0	0.0	0.40	1.28
SAR	0.21	0.32	53.0	178.1

Source: Herron, et al, 1980

3.13 CHEVRON STB OIL SHALE RETORTING

3.13.1 Retorting Operation

Details of Chevron's retorting technology have not been revealed, but a recent U.S. Patent to Chevron, No. 4,199,432 entitled "Staged Turbulent Bed Retorting Process" may give some insight into the process [DRI, SAI and KSC, 68-03-2795].

The Staged Turbulent Bed (STB) Retort is a small-particle retorting process in which retorted shale is burned in a separate combustor and recycled to the retort to supply the process heat requirement. The flow scheme for the core of the process is shown schematically in Figure 3.13-1 [Tamm et al., May 1981].

The environment in the retort section can best be described as a staged, moving bed of particles, in which a portion of the particles are "fluidized." Solids move downward through the retort with an average velocity of 2-5 ft/min. Proprietary internals within the retort restrict mixing in the vertical dimension and thereby produce "staging" of the solids flow. The "staging" gives an approach to plug flow for the solids and thereby improves the stripping action of the countercurrent gas flow and minimizes the residence time required to assure complete retorting. Locally, conditions within the bed have all the appearances of fluidized state, although the superficial gas velocity is far below the minimum fluidization velocity of many of the particles. Rapid local mixing and a high rate of heat transfer keep the temperature profile in the retort very nearly isothermal.

The retort can be operated with a stripping gas consisting of either recycled product gas, steam, or an inert gas. The superficial gas velocity at the bottom of the retort is within the range of 1-5 ft/sec. The volumetric flow of gas in the retort increases significantly in going from the bottom to the top because of the vapor traffic added by the pyrolysis products.

The combination of thermal shock experienced by the fresh shale on entering the retort, removal of the binding kerogen, and the turbulent conditions within the retort causes some breakup of the shale. The finest particles (<200 mesh) are swept overhead from the retort with the product vapors. Most of the elutriated particles are recovered from the vapor stream before condensation of the oil. The recovered particles, collected by primary and secondary devices, contain carbonaceous residue; and they are, therefore, sent to the combustor section for recovery of their fuel value.

In the product recovery section, the product vapors are condensed in stages producing several oil fractions and foul water. The initial condensation stage has to be capable of handling some

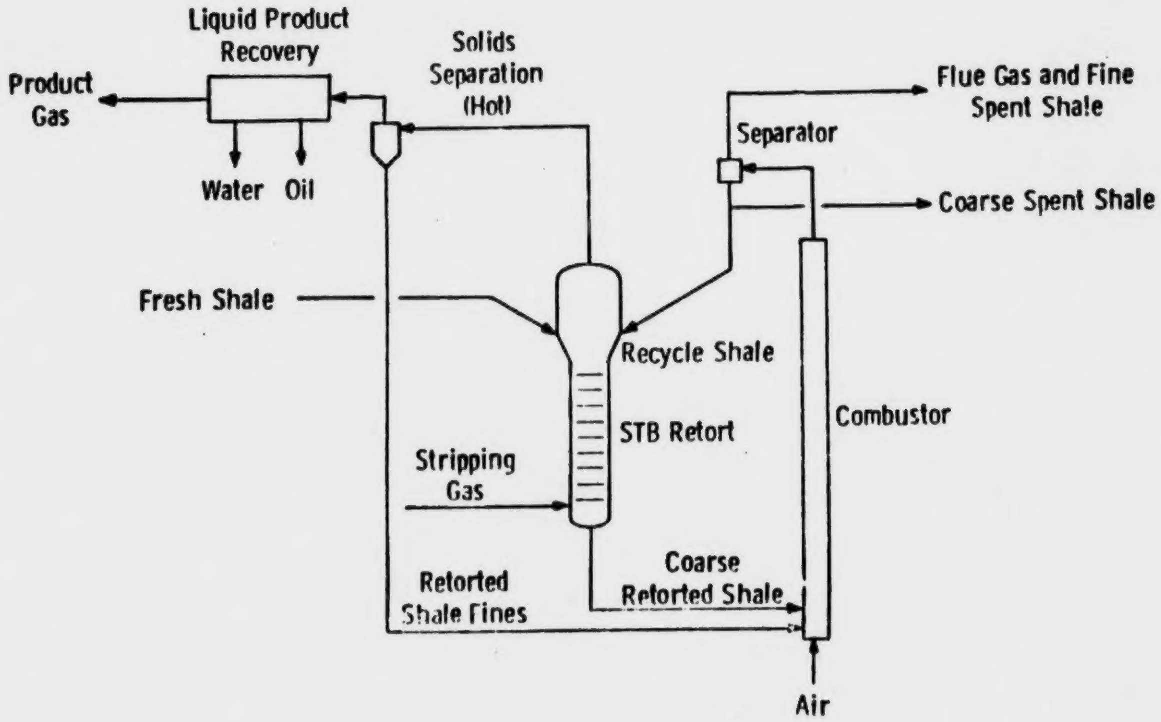

Liquid Product Recovery
Product Gas
Water
Oil
Solids Separation (Hot)
Flue Gas and Fine Spent Shale
Separator
Coarse Spent Shale
Fresh Shale
Recycle Shale
STB Retort
Combustor
Stripping Gas
Retorted Shale Fines
Coarse Retorted Shale
Air

Figure 3.13-1. Process flow scheme of Chevron STB retort.

Source: Tamm et al., May 1981

solids, as the fines removal equipment is never 100% efficient. The noncondensable gases are either produced directly or a portion is recycled to the retort for stripping. With very lean shales, some or all of the product gas can be used as a supplemental fuel in the combustor.

The combustion section receives coarse retorted shale withdrawn from the bottom of the retort and retorted shale fines removed from the product vapors. Air injected at the bottom of the combustor both transports the shale pneumatically and combusts the carbonaceous residue. The temperature of the solids rises rapidly. At the outlet of the combustor, a solids separator splits the stream once again into fine and coarse fractions. Most of the hot, coarse fraction is recycled to the retort to provide the necessary process heat. The excess coarse shale is sent on to the heat recovery section, from which it eventually discharges as net coarse spent shale. The fine fraction exits the separator with the flue gas. This stream is also sent to the heat recovery section where it is cooled and then separated into a net fine spent shale stream and a flue gas stream. The SO_x content of the flue gas is claimed to be unusually low (<20 ppm) because of the scrubbing action of the shale itself.

Nominal operating conditions for the process are summarized in Table 3.13-1. The fresh shale throughput for this process is 5-10 times that of most other retorting processes. The use of small shale particles, the excellent heat transfer conditions in the retort, and the "staging" effect in the retort make the residence time required for complete retorting quite low. The extremely low residence time required in the combustor is a consequence of the high reactivity of the carbonaceous residue.

The STB Retorting Process has been tested by Chevron Research in several pilot units including a one-ton/day integrated pilot plant. In 1984 Chevron commenced testing at a 350 ton/day semiworks plant in Salt Lake City in Utah. Figure 3.12-2 is a simplified block flow diagram for the semiworks facility adjacent to Chevron's Salt Lake refinery. The oil shale feed for the semiworks unit is obtained from the Chevron property in Piceance basin in Colorado.

3.13.2 Solid Wastes

In the retorting process, the spent shale produced is a hot dry powder. Treated process water will be used to moisten the spent shale. The moistened spent shale leaving the pugmill will have between 10 and 25% water on a dry basis.

According to Chevron's Final Environmental Impact Statement [BLM, September 1983], wastewater generated from the process plant and ancillary facilities would include effluent from the oil separation unit, cooling tower and boiler blowdown, clarifier sludge,

TABLE 3.13-1. NOMINAL PROCESS OPERATING CONDITIONS FOR THE CHEVRON STB RETORT

Fresh Shale Throughput	2000-5000 Lb/hr/ft^2 Retort
Retort Temperature	890-950°F
Retort Residence Time	2-8 Min.
Stripping Gas Velocity	1-5 Ft/Sec.
Combustor Residence Time	1-5 Sec.
Combustor Outlet Temperature	1100-1500°F
Recycle Shale Ratio	2:1 to 5:1

Source: Tamm et al., May 1981

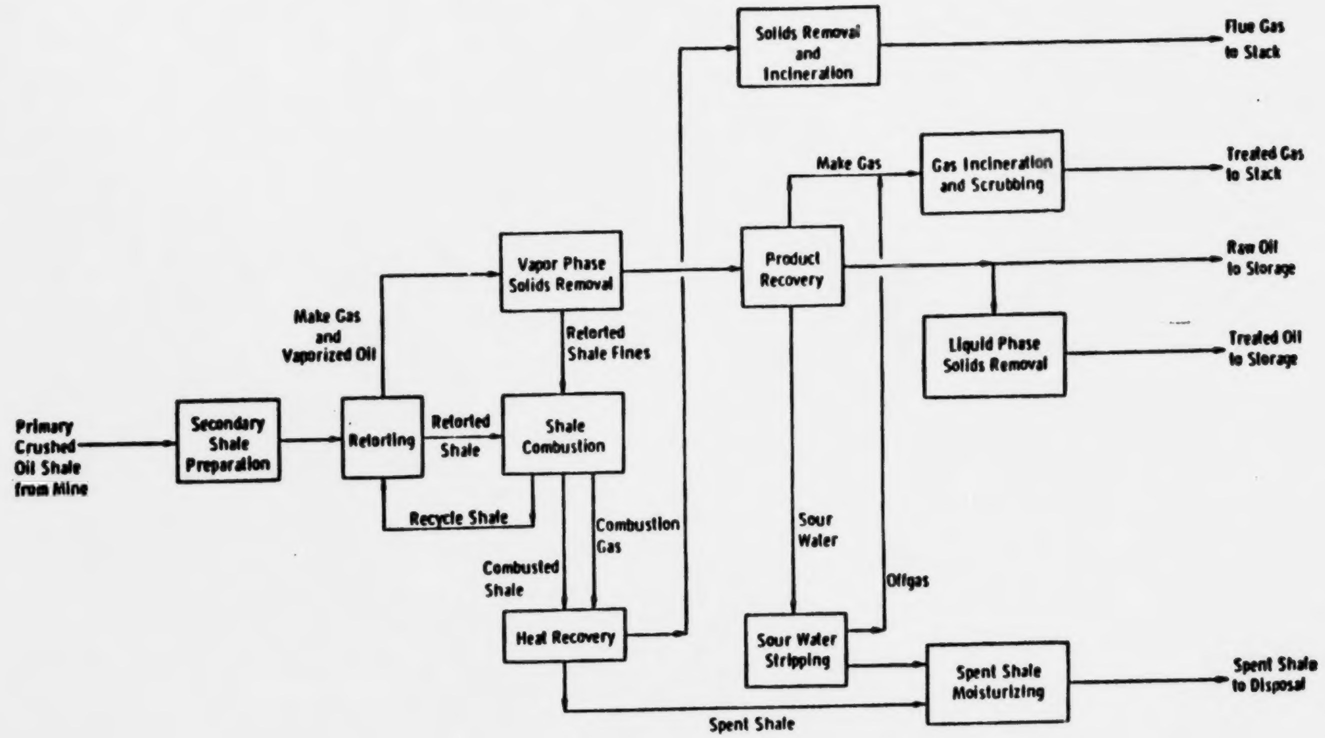

Primary Crushed Oil Shale from Mine
Secondary Shale Preparation
Retorting
Make Gas and Vaporized Oil
Retorted Shale
Recycle Shale
Vapor Phase Solids Removal
Retorted Shale Fines
Shale Combustion
Combustion Gas
Combusted Shale
Heat Recovery
Spent Shale
Solids Removal and Incineration
Flue Gas to Stack
Product Recovery
Make Gas
Gas Incineration and Scrubbing
Treated Gas to Stack
Raw Oil to Storage
Liquid Phase Solids Removal
Treated Oil to Storage
Sour Water
Sour Water Stripping
Offgas
Spent Shale Moisturizing
Spent Shale to Disposal

Figure 3.13-2. Block flow diagram of Chevron semiworks oil shale plant.
Source: Tamm et al., May 1981

filtration backwash, demineralizer waste, wash waters from boiler feedwater treatment, sour water from retort and upgrading facilities, and sanitary wastewater. All collected waters would be sent through the water treatment system before being used for spent shale conditioning.

3.13.3 Characteristics of Solid Wastes

The chemical and physical properties of the spent shale [Chevron, May 1981] are presented in Table 3.13-2. The information was generated during process development tests using Anvil Point Oil Shale. It is anticipated that the spent shale produced using shale from the Chevron property will have similar properties. Calcite and feldspars comprise approximately one-half of the shale, depending on the feed source. The physical properties of the spent shale, important in the disposal, are primarily a function of moisture content though degree of compaction and curing are factors. Permeability, dry density and unconfined compressive strength data are also presented in the foregoing Table. The chemical and physical data shown are characteristic of the material to be disposed. The results of leachate testing conducted on spent shale samples from the Clear Creek Shale Oil Project are presented in Table 3.13.3.

TABLE 3.13-2. PRELIMINARY RESULTS: CHEVRON STB PILOT PLANT SPENT SHALE PROPERTIES

RCRA EP Toxicity Test		Approximate Mineral Content[a] (Before moistening)			Properties of moistened and compacted spent shale[c]		
Result	RCRA requirements for nonhazardous waste	Mineral designation	Formula	Wt %	Strength		
Passes	As-5 ppm Maximum	a-Quartz	SiO_2	15	Compactive effort	12,375 Ft-Lb/Ft^3	
Passes	Ba-100 ppm Maximum	Analcine	$NaAlSi_2O_6$-H_2O	10	Cure time	14 Days	
Passes	Cd-1 ppm Maximum	Feldspars	(K,Na)$AlSi_3$08	25	Moisture Content	12%	24%
Passes	Cr-5 ppm Maximum	Calcite	$CaCO_3$	25	Dry density, Lb/Ft^3	95	97
Passes	Pb-5 ppm Maximum	Dolomite	CaMg $(CO_3)_2$2[b]	18	Unconfined compressive Strength, psi	200	450
Passes	Hg-200 ppm Maximum	Periclase	MgO	5			
Passes	Se-1 ppm Maximum	Illite	$KAl_3Si_3O_{10}(OH)_2$	Trace			
Passes	Ag-5 ppm Maximum						

Organic Carbon Content	Permeability
Less than 1 Wt %	Permeability ranges from 10^{-2} to 10^{-7} cm/sec depending on moisture content, compactive effort, and cure time.

---

[a] Analysis by x-ray diffraction. Mineral content will vary with feed source.

[b] Contains some Fe^{II} substitution for Mg ("Ankerite").

[c] Spent shale will be moistened in the STB process.

Source: Chevron, May 1981

TABLE 3.13-3. CHEVRON STB SPENT SHALE LEACH TEST RESULTS

	Run 45 A[a]	Run 45 B[b]
Sulfur Species		
H_2S (Hydrogen Sulfide)	3.5	1.1
Thiol	30	4.2
Sulfate	3,250	1,133
Thiosulfate	140	21
CN (Cyanide)	1	4.5
Nitrogen		
NH_3 (Nitrate)	415	37
Metals		
Antimony	0.03	0.03
Arsenic	0.03	0.01
Barium	0.2	0.3
Beryllium	0.01	0.01
Boron	3.2	1.9
Cadmium	0.03	0.03
Chromium	0.02	0.02
Copper	0.05	0.03
Iron	0.1	0.1
Lead	0.12	0.05
Mercury	1 ppb	1 ppb
Nickel	0.08	0.04
Potassium	NA	NA
Sodium	1,700	84
Selenium	0.03	0.02
Silver	0.02	0.01
Thallium	0.1	0.1
Zinc	0.14	0.01
General Water Quality		
BOD (Biochemical Oxygen demand)	500	80
COD (Chemical Oxygen demand)	1,100	120
TDS (Total dissolved solids)	10,900	4,120
TSS (Total suspended solids)	14	15
O and G (oil and grasses)	12	12
Chloride	17	5.5
Calcium/as $CaCO_3$	85/212	180/450
Magnesium/as $MgCO_3$	0.06/0.24	0.12/048
Hardness	212	450
CO_2 (Carbon dioxide)	26	6
pH	10.9	10.8
Organics		
TOC (Total organic carbon)	660	230
Phenol	18	

[a] A=First 1280 ml collected (1 pore volume)

[b] B=Third 1280 ml

[c] ND-Not detected, below detection limits

Source: BLM, September 1983

3.14 ALLIS-CHALMERS OIL SHALE RETORTING

3.14.1 Roller Grate Retorting Operation

The Allis-Chalmers approach [Faulkner et al, 1983] to the retorting of oil shale is shown in Figure 3.14-1. This is only one of many possible flowsheets that may be used depending on the shale grade and type. Raw shale with a size distribution of 1-3/4" x 1/4" enters the Preheat Zone after a minimum amount of crushing and screening. Minus 1/4" material generated in the crushing circuit is agglomerated and fed on top of the crushed material. The shale is conveyed by a series of closely spaced, slotted rollers rotating in the same direction. Beds up to three feet deep are used.

In the Preheating Zone the shale is heated by the off-gas from the adjacent first retorting zone. In addition to heating the shale, the energy in the gas is recovered and the light oils contained in the gas stream are condensed.

After preheating, the shale is conveyed to the first retorting zone where recycled noncondensible retort gases with a temperature in the range of 900-1000°F are induced down through the bed of shale and through the slotted rollers. In this zone and in the Preheat Zone, the oils driven off and condensed will be lighter and more heavily hydrogenated than the oils driven off in the following zone.

Upon exiting Retorting I, the partially retorted shale enters the second retorting zone where a 1200°F on-gas of recycled noncondensible retort gases is used to complete the retorting. In this zone, the heavier and less highly hydrogenated oils are evolved. At the exit of the zone, the gases are directed to Heat Exchanger I where the heat is recovered and the oils condensed.

When retorting is complete, the shale is conveyed through a sealing zone to the Combustion Zone. In the sealing zone, solid rollers are used to help the underbed windboxes to prevent mixing of the two atmospheres. The most difficult area to seal is at the top of the bed. This is accomplished by using hinged drag plates at the entrance and exit of the Sealing Zone and by maintaining equal overbed pressures. In the combustion zone, the residual carbon and hydrogen are combusted with ambient air to recover energy for driving the retorting process. Contrary to the proceeding three zones, air flows up through the rollers and exits from the top of the bed. By doing this, the mechanical elements are not exposed to the hot off-gas and a low temperature fan is used to blow ambient air through the bed.

After removal of the thermal energy in the Combustion Zone, the shale proceeds to the Cooling I Zone where the shale is cooled and its sensible heat is recovered by an ambient air stream. Final cooling of the shale to an acceptable discharge temperature is performed in the Cooling II Zone also with ambient air.

The hot off-gas streams from the Combustion and Cooling I Zones are combined and sent to Heat Exchanger II where the heat is transferred to the recycled retort gases used in the retorting zones. Depending on the grade of shale and its carbonate content, a portion of the retort gases generated may need to be combusted to achieve adequate heat transfer in the second heat exchanger. A portion of the reheated retort gases coming from Heat Exchanger II are sent directly to Retorting II. The remainder is blended with the reheated retort gases from Heat Exchanger I and are used as the on-gas for Retorting I.

Commercial Roller Grate Retort modules have been designed with a raw shale capacity of 20,000 TPD which results in the need of only three such modules in parallel to produce 43,000 BPD of oil from a 30 GPT shale. Such a device would have an active width of 15 feet and a working length of 500 feet.

The size of the raw feed shale is a trade-off between the benefits of a small shale size and costs associated with obtaining that size and disposing of the fine shale. The Allis-Chalmers process uses the largest size that can be efficiently processed. Undersize material that results from the crushing operation can be agglomerated into flakes and fed directly to the top of the shale bed. Tests have confirmed that these agglomerates maintain their integrity throughout the entire retorting and combustion process.

The rollers used to convey the bed of shale give it relative motion along with causing a natural size segregation to occur. The relative motion keeps exposing fresh shale surface and allows the theoretical heat transfer potential to be achieved. Fines carried in with the feed quickly migrate to the bottom of the bed and fall into the underbed windbox. This prevents pockets of fines from forming and causing gas channeling. Natural size segration puts the larger particles on top and the smaller on the bottom of the bed. Thus the downdraft retorting gases give the largest thermal driving force to the particles that need it the most.

For any process to reach its maximum efficiency, the residual carbon and hydrogen in the retorted shale must be utilized. The energy contained in these components amounts to 10-15% of the energy in the raw shale. In the Allis-Chalmers process ambient air alone is used to combust the residual carbon and hydrogen. The excess air to the Combustion zone along with the moderating effect of the calcination reaction prevent unacceptable temperatures from being reached. In the case of a very high grade shale with a higher level of residual carbon and hydrogen, a tempering gas such as recycled heat exchanger II off-gas can be used. The retorting gases used in the Roller Grate Retorting Process are the recycled gases generated from the decomposition of the kerogen.

Tests have shown that the fully combusted and cooled shale exiting the Allis-Chalmers Process still maintains its integrity. Fines generated in processing represent a small fraction of the total feed. Residual carbon in the combusted shale is less than 1%.

A Roller Grate Process Development Unit was designed and built. This unit is capable of processing charge weights up to 1500 lbs with bed depth up to 21 inches. It is designed to simulate the process from raw shale to fully combusted spent shale. A schematic of the entire system is shown in Figure 3.14-2.

Table 3.14-1 depicts results for a typical test starting with raw shale continuing through retorting and combustion and ending with fully processed and cooled spent shale. During a test less than 0.2% of the raw shale was carried out of the retort as dust. A relatively small 1.1% of the shale reported to the windbox as fines. Size analysis comparison between the raw and fully combusted shale showed that there was very little size degradation during processing. Agglomerated fines also maintained their integrity after retorting and combustion.

It should, however, be emphasized that studies by Allis-Chalmers have been limited to process development unit (PDU) bench scale, batch equipment only. The system has not been tested in any continuous retorts; the 500 TPD and 60,000 TPD units have not been built and operated. Also no demonstration units have been built or operated.

3.14.2 Solid Wastes

There is no information on this subject.

3.14.3 Characteristics of Solid Wastes

There is no information on this subject.

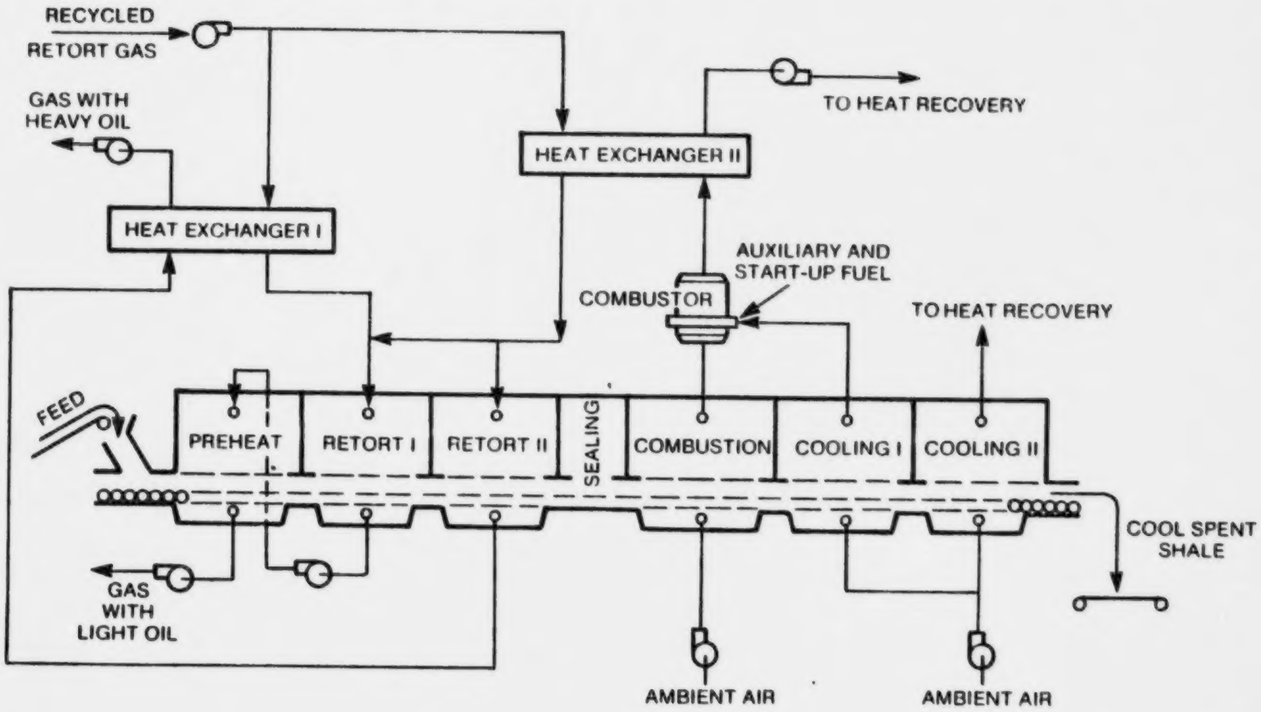

RECYCLED
RETORT GAS
GAS WITH
HEAVY OIL
HEAT EXCHANGER I
HEAT EXCHANGER II
TO HEAT RECOVERY
AUXILIARY AND
START-UP FUEL
COMBUSTOR
TO HEAT RECOVERY
FEED
PREHEAT
RETORT I
RETORT II
SEALING
COMBUSTION
COOLING I
COOLING II
COOL SPENT
SHALE
GAS
WITH
LIGHT OIL
AMBIENT AIR
AMBIENT AIR

Figure 3.14-1. Allis-Chalmers Oil Shale Process Flowsheet. Source: Faulkner et al., 1983 (Reprinted from Sixteenth Oil Shale Symposium Proceedings by permission of Colorado School of Mines Press.)

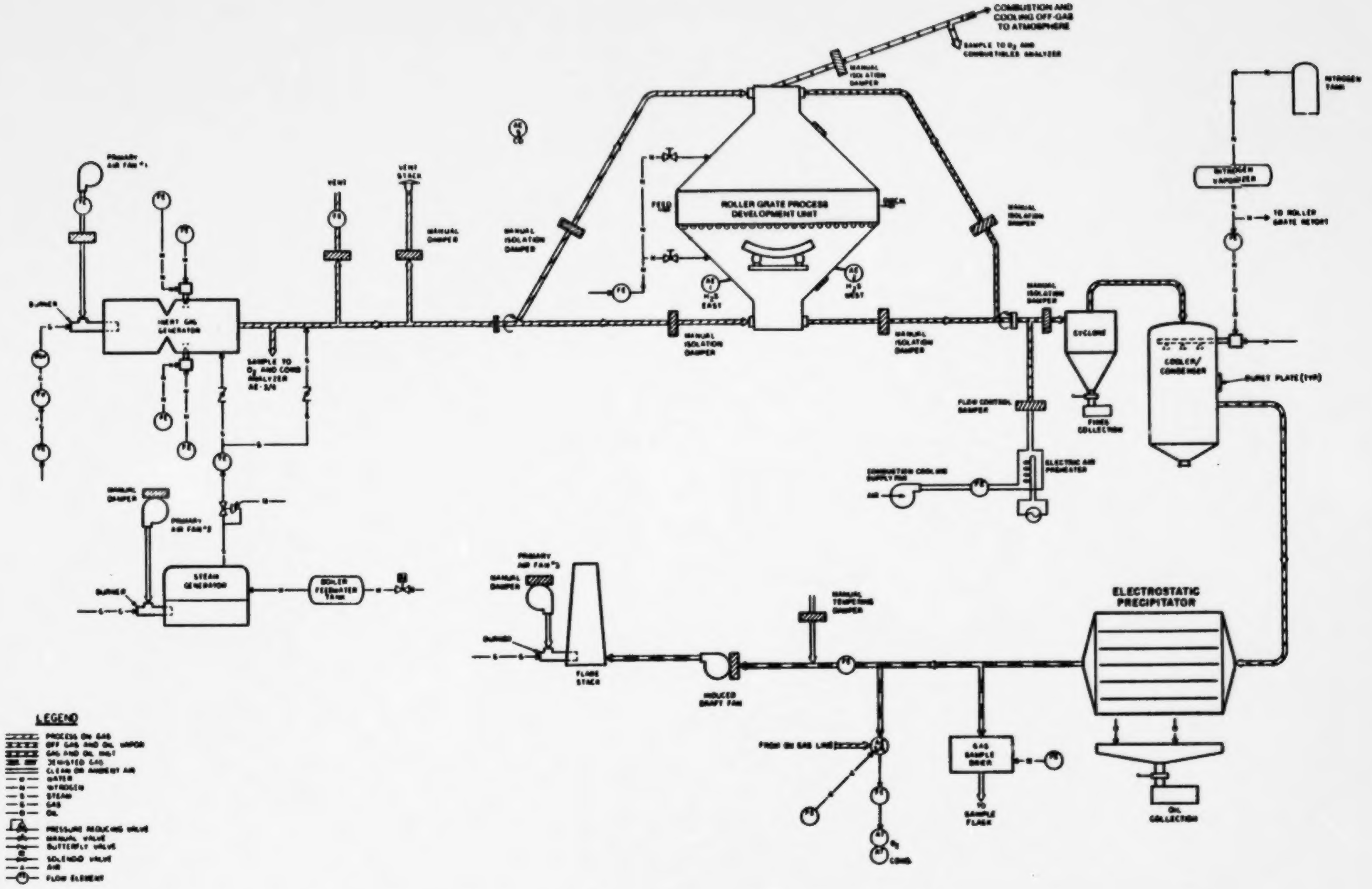

COMBUSTION AND COOLING OFF-GAS TO ATMOSPHERE
SAMPLE TO O_2 AND COMBUSTIBLES ANALYZER
MANUAL ISOLATION DAMPER
NITROGEN TANK
NITROGEN VAPORIZER
TO ROLLER GRATE RETORT
PRIMARY AIR FAN #1
VENT
VENT STACK
MANUAL DAMPER
MANUAL ISOLATION DAMPER
FEED
ROLLER GRATE PROCESS DEVELOPMENT UNIT
MANUAL ISOLATION DAMPER
BURNER
INERT GAS GENERATOR
SAMPLE TO O_2 AND COMB ANALYZER AE-3/4
H_2S EAST
H_2S WEST
MANUAL ISOLATION DAMPER
MANUAL ISOLATION DAMPER
MANUAL ISOLATION DAMPER
CYCLONE
COOLER/ CONDENSER
BURST PLATE (TYP)
FLOW CONTROL DAMPER
FINES COLLECTION
ELECTRIC AIR PREHEATER
COMBUSTION COOLING SUPPLY FAN
AIR
MANUAL DAMPER
PRIMARY AIR FAN #2
BURNER
STEAM GENERATOR
BOILER FEEDWATER TANK
PRIMARY AIR FAN #3
MANUAL DAMPER
BURNER
FLARE STACK
INDUCED DRAFT FAN
MANUAL TEMPERING DAMPER
ELECTROSTATIC PRECIPITATOR
FROM OH GAS LINE
GAS SAMPLE DRIER
TO SAMPLE FLASK
OIL COLLECTION
O_2
COMB.
LEGEND
PROCESS OH GAS
OFF GAS AND OIL VAPOR
GAS AND OIL MIST
DEMISTED GAS
CLEAN OR AMBIENT AIR
WATER
NITROGEN
STEAM
GAS
OIL
PRESSURE REDUCING VALVE
MANUAL VALVE
BUTTERFLY VALVE
SOLENOID VALVE
AIR
FLOW ELEMENT

Figure 3.14-2. Allis-Chalmers Oil Shale Retorting and Combustion Process Development Unit Flow Schematic. Source: Faulkner et al., 1983 (Reprinted from Sixteenth Oil Shale Symposium Proceedings by permission of Colorado School of Mines Press.)

TABLE 3.14-1. ALLIS-CHALMERS WESTERN SHALE TESTS
Basis: 100 kg dry raw shale

	Total	Carbon	Sulfur
IN			
Dry raw shale	100.0	11.7	1.33
OUT			
Residual solids	74.2	0.5	0.90
Windbox fines	1.1	-	-
Cyclone fines	0.2	-	-
Dry gas produced	2.1	1.1	0.35
Water produced	1.5	-	-
Oil produced	9.9	8.3	0.10
Co_2 calcined in retorting	1.2	-	-
CO_2 calcined in combustion	8.0	-	-
Carbon combusted	1.8	1.8	-
Sulfur combusted	0.01	-	0.01
TOTAL	100.0	11.7	1.33

[a] Oil produced: 100% of Fischer assay.

[b] Organic removal: 97% of initial kerogen

Source: Faulkner et al., 1983

3.15 DRAVO OIL SHALE RETORTING

3.15.1 Retorting Operation

In the Dravo Retorting Process [Forbes & Kinsey, 1981] the raw shale is retorted on a traveling grate (Figure 3.15-1). The retorting section is divided into three parts: an initial heat-up zone; the burning of residual carbon; and initial cooling of retorted shale. The shale is then cooled for disposal. Off-gases from the retorting and cooling sections, after cooling and oil recovery, are reused in the process as heat carriers. Excess, or by-product gas, is bled from the system as necessary.

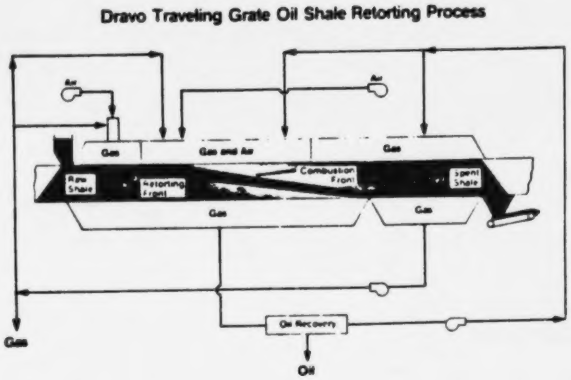

Dravo Traveling Grate Oil Shale Retorting Process
Air
Air
Gas
Gas and Air
Gas
Raw Shale
Retorting Front
Combustion Front
Spent Shale
Gas
Gas
Oil Recovery
Gas
Oil

Figure 3.15-1. Dravo Retorting Process
Source: Forbes & Kinsey, 1981
(Reproduced with permission.)

During retorting there is no relative movement between particles where abrasion could degrade the particles and disrupt the process. Free water can be removed from the shale concurrently with retorting or in a separate zone ahead of the retorting zone, if necessary.

The heating value and quantity of byproduct gas are principally determined by the amount and purity of oxygen added, the efficiency of processing, and the amount of kerogen in the shale. A heating value of 100-110 BTU/SCF is indicated in this process for 28 GPT Western oil shale. The ultimate use of air or oxygen would depend on an economic evaluation.

The weight of spent shale for a 28 GPT Colorado shale would be 83% of the shale charged to the grate. Less than 10% of the carbonate is calcined and about half the carbon is burned out. Disposal problems are not unique.

The technical feasibility of agglomerating oil shale fines and recycling solids separated from the oil was verified by Dravo. The latter processing would eliminate a difficult disposal problem. One would expect agglomeration to be used, however, only if economically viable for a given property.

Dravo's Shale Oil Pilot Plant is located in Cleveland, Ohio. It was originally constructed in 1974, and operated for several runs. It has been revamped to conform with the latest Dravo technology and shale oil recovery methods. It is a circular grate having 88 square feet of actual grate area. It can process 300 tons-per-day of oil shale. The pilot plant flowsheet (Figure 3.15-2) illustrates the basic flow scheme of this facility. Raw shale is crushed and screened. Belt conveyors move the crushed shale to the traveling grate over a weigh belt scale for material weight recording. The shale bed travels under the first retorting zone hood, which contains hot, oxygen-free, process gas. The first retorting zone covers several of the machine's 12 windboxes.

The second and third retorting zones cover additional windboxes. The second retorting zone is fed by oxygen-enriched, recycled process gas. The third retorting zone is fed with oxygen-free process gas. The air that is injected into the second retorting zone hoods causes combustion of shale carbon to provide the heat for further retorting. At the discharge end of the retort zone 100% of the oil has been extracted from the shale, approximately 50% of its carbon has been burned, and a significant percentage of the shale has been cooled. The cooling zone consists of the last several windboxes which has been fed with cool, oxygen-free process gas. The shale is then conveyed to the discharge area where the pallets are tipped and the shale falls into a water-sealed discharge hopper. A belt conveys the shale to a refuse pile for ultimate disposal. The retort gases are collected in windboxes and ducted to an oil recovery system.

3.15.2 Solid Wastes

There is no information on the subject.

3.15.3 Characteristics of Solid Wastes

There is no information on the subject.

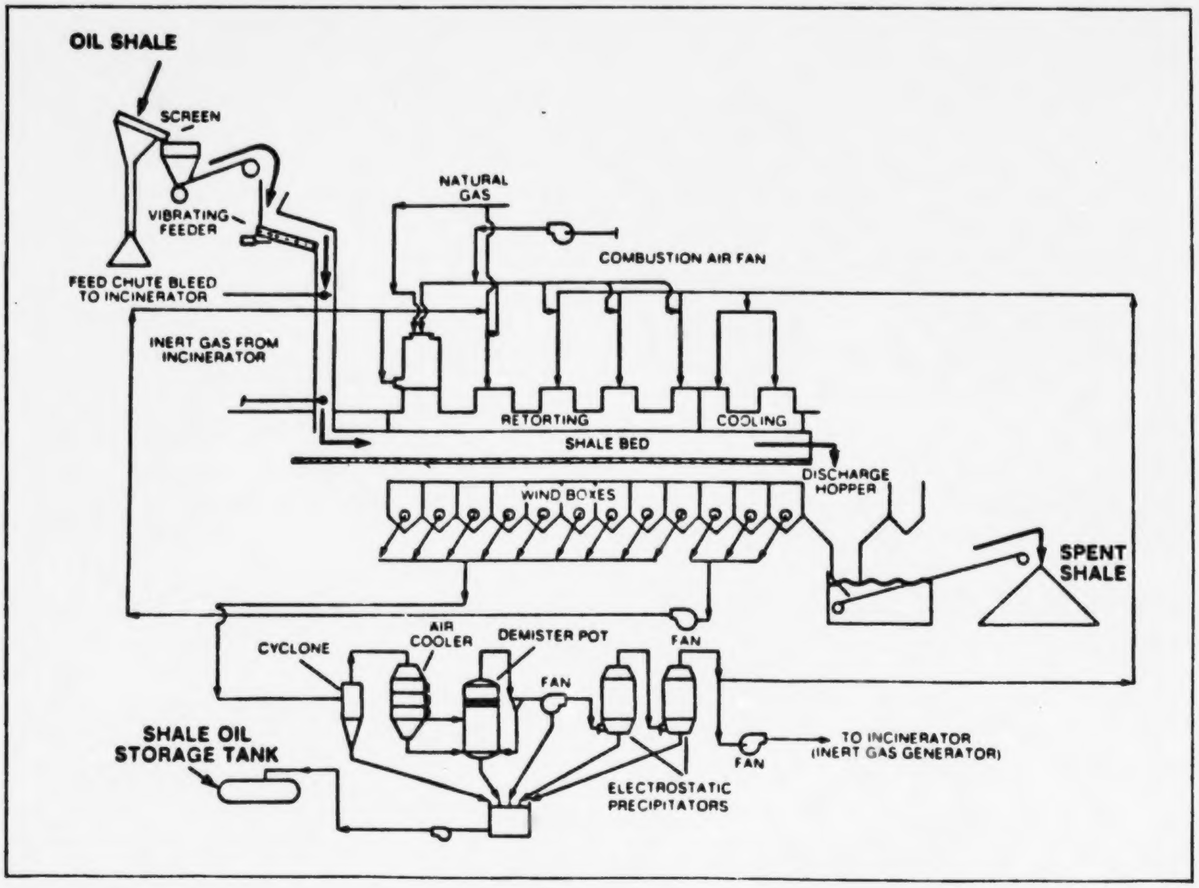

OIL SHALE
SCREEN
VIBRATING FEEDER
NATURAL GAS
COMBUSTION AIR FAN
FEED CHUTE BLEED TO INCINERATOR
INERT GAS FROM INCINERATOR
RETORTING
COOLING
SHALE BED
DISCHARGE HOPPER
WIND BOXES
SPENT SHALE
CYCLONE
AIR COOLER
DEMISTER POT
FAN
FAN
FAN
TO INCINERATOR (INERT GAS GENERATOR)
SHALE OIL STORAGE TANK
ELECTROSTATIC PRECIPITATORS

Figure 3.15-2. Dravo Pilot Plant Flowsheet Schematic
Source: Forbes & Kinsey, 1981 (Reproduced with permission.)

SECTION 4

ENVIRONMENTAL CONTROL TECHNOLOGIES

4.1 ENVIRONMENTAL IMPACTS

4.1.1 Introduction

An oil shale operation will result in significant land disturbance on and near the development site [DRI, SAI & KSC; 68-03-2795]. Land will be required for access to the site for mining, processing facilities, and for waste disposal, all of which will permanently modify the surrounding terrain and influence the ecosystem by causing changes in the vegetation and habitat. Local aesthetics will also be affected.

The most prominent impacts will probably result from the disposal of the shale wastes. Unlike potential impacts on air and water systems, the solid waste impacts will linger long after a mine has been depleted and the shale processing facility is closed down. For this reason, the measures taken for mitigating the impacts of solid waste disposal must withstand a minimum test of time, without the possibility of a breakdown.

One factor of paramount importance in the disposal of the solid wastes is the surface and groundwater regime of the site. While a waste landfill should blend in cosmetically with the surroundings, so that its existence can go practically undetected, it should be sufficiently isolated from the surrounding strata so that the hydrologic environment is protected. Other factors influencing the waste disposal and land disturbance impacts are the scale and duration of the oil shale operation, and the mining and retorting technologies used.

The surface and subsurface impacts will vary depending upon the waste disposal approach used. Available disposal methods are canyon or valley fill, surface landfill, open pit backfill, underground mine backfill and least likely, a commercial market for waste utilization. Selection of any of these approaches, or their combination, is largely dependent on the site-specific features, mining method used, and the properties of the processed shale (retorting method used).

4.1.2 Raw Shale Mining and Handling

A substantial amount of raw shale would need to be mined and processed to produce oil. This is primarily because the oil shale can be considered as a low-grade ore. A Mahogany Zone oil shale averaging 26 gal/ton contains approximately 17 percent kerogen by weight, of which about 75 percent can be converted to oil (~13 percent of the raw shale weight). An oil shale plant producing 66,700 bbl/day of crude shale oil from the 26 gal/ton shale will need to process 70,000 ton/day of raw shale as a minimum (at 100 percent of Fischer assay yield). This is a large quantity by the existing standards of the mining industry.

The shale handling will include blasting, conveying, stockpiling and several stages of crushing to prepare the feed for the retorts. The particulate control operations will produce raw shale fines which cannot be retorted by many of the retorting processes therefore, they must be disposed. The preheat system of the TOSCO II process produces a raw shale sludge which also must be discarded. As much as 10 percent of the mined out shale (or 7,000 ton/day for 66,700 bbl/day production) may be disposed of in the case of Paraho, while the raw shale waste for the TOSCO II process may range from 1.5 to 2 percent of the run-off-mine shale (or 1,000 to 1,400 ton/day). When compared with the amount of the processed shale (e.g., 80 percent of the raw shale weight, or 56,000 ton/day), the raw shale quantities seem insignificant, but they will increase the carbon content of the waste piles. For the Paraho direct-heated, processed shale, the carbon content will change from an initial 2 percent to approximately 3 percent, or a 50 percent increase in the amount of carbon. The impact on TOSCO II processed shale is less significant, because of its already high carbon content. This increase in the carbon value, nonetheless, increases a potential for volatiles release from the waste pile, in the event that self-heating (autooxidation) occurs within the pile. The physico-chemical impact of mixing the raw and processed shales is unknown. There could be problems with the waste pile stability or increased permeability, hence leaching.

Several conceptual measures are available for mitigating the impact of raw shale disposal. The raw shale can be disposed of separately from other wastes. This approach can have its own problems as additinal maintenance and monitoring may be required, but they should be easily manageable due to the much smaller size of the raw shale disposal pile. It would also allow future recovery of the resource. The resource recovery simultaneous with the processing, however, may be a preferred approach, because it will not require the additional handling of the raw shale. Several alternatives can be pursued and developed regarding the utilization of the shale fines. The fines can be briquetted into larger pieces, then processed by the same retorting technology. Another option is to have a small fines handling retort on the site. Current thinking by some oil shale developers is to burn the fines in a fluidized bed or lift pipe and utilize the energy to provide process heat and steam. The process fuels saved by this approach can be put to better use or sold commercially.

4.1.3 Processed Shale Handling and Disposal

The processed shale will be the major waste produced by oil shale processing; therefore, its disposal will be of primary concern. The vast quantities of the processed shale produced may make its safe handling and disposal the greatest environmental issue of oil shale processing. The environmental repercussions can be long lasting; therefore, utmost care should be taken before implementing any long-term plans. To the extent possible, the processed shale disposal should occur in such a manner as to return the disturbed land to its original state of landscape, use and biological productivity. This would require proper handling and disposal practices, protection of air and water quality and surface reclamation.

The physical and chemical properties of the processed shale will be the determining factors in the selection of disposal and reclamation approaches. Every retorting method produces a processed shale that is unique in quality, and every development site has features not found elsewhere; therefore, their combination should be analyzed on an individual basis. The physical and chemical characteristics of the processed shale are determined by the source of the raw shale, its particle size after crushing and retorting, the retorting parameters, and most importantly, the temperature of retorting.

There are primarily two types of processed shale--carbonaceous and burned (decarbonized). Carbonaceous processed shales are produced by indirect retorting in which residual coke on the retorted material is not incinerated. Examples of this type of retorting are the TOSCO II and Union B processes. Burned shales originate either from direct-heated processes, such as Paraho and Modified *In Situ* (MIS), in which the air is introduced in the retort to cause combustion of the residual carbon, or from combination-mode processes, such as, Lurgi Superior and Union C, in which the retorting primarily occurs in the indirect-mode, but the residual coke on the processed shale is incinerated in a separate stage.

The carbonaceous processed shales have usually been subjected to low enough temperatures (980°F) so that significant calcination and other mineral transformations do not occur. These type of shales normally yield less water soluble material than burned shales but have poor cementation properties which result in increased water permeability, hence leaching. The burned shales (1290-1830°F), indicate considerable calcination and mineral transformation. As a result, they behave more like Portland cement and thus form an impermeable mass upon wetting and setting.

Once penetrated, however, usually more water soluble material may be leached out than can be leached from carbonaceous processed shales.

The particle size, or the texture of the processed shale, also has significant impact on the physical properties. The TOSCO II and Lurgi processes use finely crushed raw shale as the retort feed. In the former process, the shale is further divided due to the ball-milling action in the retort. Some disintegration of the Lurgi processed shale occurs in the lift pipe and recycle loop. As a result, both of these processes produce an even finer, silty processed shale. Although better compaction, cementation, and lower permeability are obtained with the fine material, the potential for erosion due to wind and run-off is increased. The Union B, Superior, and Paraho processes use rather coarse shale for retorting. Accordingly, the processed shale also has a coarse texture. While resistant to erosion, the coarse material does not have good cementation properties and water permeability is higher. The characteristics for some of these processed shales have been discussed in Section 3.

4.2 DISPOSAL ALTERNATIVES

The mining and processing of oil shale actually results in an increase in the volume of the shale. In-place density of the raw shale is approximately 2.16 g/cm^3, but the processed shale can be compacted to only about 1.6 g/cm^3 by practical means. Even after losing about 20 percent of the original weight, which is a reasonable assumption, the shale after retorting will occupy about 10 to 15 percent more volume than it originally occupied. This is an important factor when considering different approaches for the processed shale disposal.

Processed shale moisturizing will be an essential ingredient in disposing of the processed shale. It will serve numerous functions. The processed shale will emerge from most retorts at an elevated temperature; therefore, it will require cooling and/or moisturizing prior to handling and disposal. Transportation of the processed shale to the disposal area will involve extensive materials handling and transfers which are potential sources of airborne particulates. The particulate emissions can be minimized, by moisturizing and using covered transport. Perhaps the most significant advantage of moisturizing is in obtaining proper compaction, and cementing reaction, which in turn will allow disposal of a maximum quantity of the material in a given space and will provide greater stability to a waste landfill.

Several alternatives are available for the disposal of the shale processing wastes. The mining and retorting methods used, geography of the disposal site, and the surface and subsurface hydrology of the area will dictate the selection of the disposal approach(es).

Surface landfill--Disposal in a valley or canyon near the plant site may be the preferred approach by many oil shale developers. This selection is influenced by the rugged terrain of the oil shale areas in Colorado and Utah. Usually, large valleys and/or canyons are available on the development sites to accomodate the wastes generated throughout the operational life of the projects.

With proper reclamation the landfill can be blended into the surrounding terrain so that it can go unnoticed. The landfill can be built as deep as the valley or canyon so that the bulk of the material is protected from the weather. Additionally, this would reduce the surface area that would need to be reclaimed or revegetated. Water contamination due to run-on and run-off, and mechanical failure due to mass movement and slippage are some adverse possibilities in this type of landfill.

To avoid or reduce the mechanical instability, the face of the pile should be built at an angle well below the internal angle of friction. The laboratory data for most processed shale would indicate that a waste pile with a 2:1 slope (2 units horizontal for every unit vertically, or approximately a 27° angle) would be mechanically stable, but potential operational safety, erosion and revegetation problems suggest that the slope should be no steeper than 3:1 and possibly 4:1.

If the disposal area is flat, then the landfill would need to be built above the surface. This type of waste pile will not blend into the surrounding environment and will be visible from a distance. The run-on and run-off problems would be limited and perhaps, easily manageable. The pile-up operations may be somewhat difficult when compared with the valley fill operations. Also, exposure to wind and water may result in excessive erosion.

Solid waste management employs several integrated controls and practices. Techniques for controlling erosion due to wind and water, controlling natural water contamination due to run-off and leachate, controlling permeability through the waste pile, run-on and run-off diversion, leachate collection, monitoring, revegetation, etc., are employed to mitigate the adverse impacts of the solid waste disposal.

The processed shale and other processing wastes, when disposed of in a surface landfill, will be exposed to rain, snow, and wind. These natural forces will disturb or erode the waste particles on the surface. Upon disturbance, these particles may either become airborne or may be carried with the run-off. While a direct impingement of the wind and water on the waste pile is unavoidable, the erosion can be minimized by proper sloping and compaction, surface stabilization and vegetation. Surface stabilization consists of the application of water or chemical spray, or the addition of emulsified asphalt or limestone. These techniques help in binding particles together and in hardening the surface, thereby minimizing erosion.

Depending upon the surface permeability, the impinged water will run off the pile, infiltrate the pile, or both. The water can infiltrate the waste pile by permeation through the surface and/or by channeling through cracks and other artifacts. In such an event, the potential of leaching the water soluble material from the waste is greatly increased. In the case of more permeable, coarse processed shales, some fines can be added to fill the void spaces, thereby reducing the water permeability. Creating an impervious cover on the surface of the waste pile using a processed shale/ soil-cement mixture can also reduce the water permeability. Several feet of plant growth medium would then have to be placed on top of the cover in order to vegetate the pile. Low precipitation and high evaporation rates in the semi-arid oil shale area help to minimize the potential of leaching.

Water flow diversion and collection structures would greatly reduce the erosion and leaching potential. The waste piles would be built in benches, perhaps 50 ft. high. Each bench can then be backsloped into a drainage system at the base of each bench. The runoff from a section of the bench would be collected by the drainage system rather than letting the run-off flow onto the next bench.

Similar collection and diversion systems can be built around the waste pile at the junction of the pile and the surrounding strata, to divert any run-on, thus preventing its contact with the waste.

Catchment basins at the bottom and perhaps above the landfill, are practically essential for any surface landfill. While the pile impermeability is preferred in order to reduce the leachate potential, it will increase the run-off potential. The uncontaminated run-on can be collected in the catchment pond above the pile, reducing the quantity of water to run off the pile. This uncontaminated water can be diverted around the landfill into natural drainage.

The catchment pond at the base of the pile will collect the contaminated run-off. The area of this basin should be large enough so that the average evaporation rate is higher than the average in-flow rate and be designed with a capacity for containing the run-off from major (100 year) storms. The basin should be lined with impervious material to prevent infiltration.

In the event of excess water collection in the catchment basin, some mitigating measures can be taken. During the processing operations, the necessary amount of collected water can be treated to meet the discharge or underground injection standards and disposed of accordingly. Since most of the contaminants in the collected water would have originated from the waste pile, the excess water can be reused for moisturizing the process wastes and for dust suppression at the disposal site. These reuse options may reduce the overall water consumption by the plant.

Monitoring the changes in the geologic conditions of the area, groundwater quality, waste properties, etc., should be an integral part of the overall solid waste management. Any significant change in these indicators may dictate a change in disposal strategy, or replacement/repair in the built-in structures, etc. Thermocouples can be installed in the pile to monitor self-heating processes. Volatile components can also be monitored for any indications of self-heating in the pile. A sudden degradation of groundwater quality may indicate breakthrough of the leachate or run-off. A preventive cure may not be possible for all of the causes. However, retrofit measures can be taken in some case to reduce further degradation or hazard.

Open pit backfill--This method of disposal may be viewed as a type of surface landfill. As a prerequisite, the mining operation must have been performed by open pit mining to allow this type of disposal. This mining allows more resource recovery than the underground methods, but additional handling of the overburden and subore is also necessary.

The logistics of simultaneous mining and backfilling operations require that the mine be developed for 20-30 years at a commercial scale rate (100,000 ton/day) before backfilling can commence. The overburden, subore, and processing wastes generated during these years must be temporarily stored or permanently disposed somewhere else so that the full resource can be developed. Even after all the backfilling has been done, some off-site disposal may be necessary because the volume of the backfill material will be greater than the volume being created by the mining. Without additional off-site disposal, the backfilling operations will catch up with and inhibit the mining operations.

After the project shutdown some waste from the off-tract disposal can be returned to the mine, but approximately 20-30 percent of the total mined out volume would need to be stored or disposed of permanently outside the pit. By complete backfilling, the land can be brought back to its original contour. If the pit is backfilled to a level surface, a depression may later develop due to compaction and settling, allowing water collection and possible infiltration. Hence it may be desirable to pile the waste above the existing terrain. However, the surface reclamation and aesthetics, in this case, may be of inferior quality compared to the leveled backfill.

It is likely that not all of the controls necessary for a surface landfill may be required for the open pit backfill. The erosion potential will be greatly reduced, because a bulk of the material will be unexposed to the weather elements. Certainly, the catchment ponds will not be required. Use of extensive diversion and collection systems may be discontinued if original drainage patterns can be restored.

One potential problem of the open pit backfill could be groundwater contamination. If the pit intersects any existing aquifer, the waste will be placed in the course of the aquifer. After mixing when the aquifer dewatering is discontinued, the water will penetrate the waste mass and eventually saturate it.

Underground mine backfill--Return of the processed shale to the underground mine is an attractive disposal approach. Several of the problems associated with the exposed (surface) landfills will be nonexistent in the underground disposal. Since the waste would be protected from the weather, erosion potential is diminished. Surface reclamation and vegetation would be reduced. Most importantly, the danger of mine subsidence would be greatly reduced.

However, the logistics of simultaneous mining and backfilling operations could be complex and may require substantial aboveground disposal capacity. Furthermore, due to volume expansion on retorting, not all of the processed shale can be accomodated underground using practical compaction machinery. Total accomodation of the waste may be achieved if it is compacted in excess of 1.84 g/cm^3. While this magnitude of compactive effort is attainable aboveground with very large, heavy equipment, operation of such equipment would be very difficult in the underground mine.

Several underground backfilling methods are available, but none of these have been tested on a large scale. Slurry backfilling via pipelines is practical for fine processed shale disposal but not suitable for the coarse materials. This method would have the disadvantages of adding water enhancing groundwater contamination, and would require excess water collection systems. Other methods involve transportation, either by conveyors or by trucks, followed by compaction using standard machinery. Pneumatic transport is also a possibility. A combination of these methods, perhaps, would yield the best results, but realistically, not more than 60 percent of the processed shale can be returned to the mine. Release of volatiles may create a worker safety and fire hazard.

In situ retort abandonment--Even though the *in situ* retorting processes do not involve disposal of the processed shale per se, the retorted mass underground represents the shale waste that must be attended. Perhaps one can consider the spent retorts as equivalent to the backfilled underground mine. Some differences do exist, however. The groundwater seepage in an underground mine is detectable and manageable before backfilling. In the case of an *in situ* retort, the problem, if existent, must be taken care of after the retort is spent. The size and placement of the material in backfilling is controllable, while the same is not possible with the *in situ* retorts.

Of greatest concern in the abandonment of the *in situ* retorts may be the groundwater infiltration, heat retained in the retorted mass, and air leakage in the retort causing a potential for combustion hazard. The average temperature in a spent retort may be fairly high (532°F). Some retorting and/or softening of the pillars will occur reducing their structural strength. Due to the negative pressure maintained in the retorts, air inflow may occur. Furthermore, some partially retorted shale pieces may exist in the retort. A combination of these factors may lead to renewed combustion in the retort.

The spent retorts can be grouted by injecting cement slurry at high pressure in the retort. While this approach may not prevent the groundwater from entering the retort, it will slow the water permeating through the rubble and leaching the shale. Filling the voids will improve the structural strength and reduce the subsidene potential.

4.3 CONTROL TECHNOLOGIES

The following discussion is drawn principally from EPA publication [EPA-600/8-83-003, 1983] and summarizes the major control technologies to prevent contamination of surface and groundwater supplies by runoff or leachate, prevent generation of windblown dusts, and prevent mass failure of a surface landfill. The selection and application of appropriate control technologies must be done on a site and plant specific basis wherein the controls are integrated into a specific disposal design. A few specific examples of individual control technology costs have been estimated in order to provide an idea of the costs involved. The substantial cost of transporting and compacting the solid wastes are excluded from the estimated costs since these activities must be accomplished for process rather than environmental purposes.

4.3.1 Surface Hydrology Control Technologies

Solid waste management practices in the area of surface hydrology entail the handling of surface waters on and around the disposal facility. Specifically, surface streams and precipitation are prevented from running onto the waste pile, and contaminated waters (runoff, leachate) are kept from mixing with the natural waters.

The technologies discussed below are those that are applicable to a surface landfill, and they are summarized in Figure 4.3-1. The key features of the technologies are highlighted in Table 4.3-1 and a more detailed description with cost data is presented in the text.

Runon Diversion System

A runon diversion system will generally be needed with any surface landfill to prevent surface water from flowing onto the waste material and becoming contaminated or causing erosion. The system

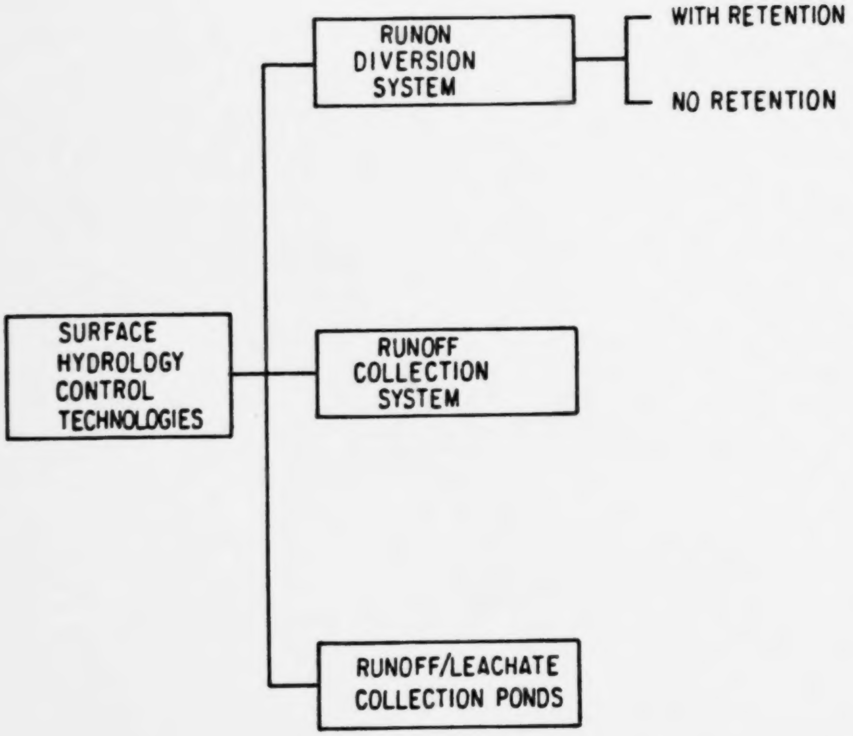

SURFACE HYDROLOGY CONTROL TECHNOLOGIES
RUNON DIVERSION SYSTEM
WITH RETENTION
NO RETENTION
RUNOFF COLLECTION SYSTEM
RUNOFF/LEACHATE COLLECTION PONDS

Figure 4.3-1. Surface Hydrology Control Technologies
Source: EPA-600/8-83-003, 1983

TABLE 4.3-1. KEY FEATURES OF SURFACE HYDROLOGY CONTROL TECHNOLOGIES

Control technology	Principle	Purpose	Comments
Runon Diversion System	Uses channels and embankments to prevent surface water from contacting the waste material.	Reduces erosion and increases site stability. Reduces the amount of water contacting the waste material, thereby reducing the potential for surface water pollution.	Reduces the amount of water contaminated, thereby reducing treatment costs.
With retention	Embankment dam holds peak flows for controlled release, evaporation, or percolation into the ground.		Requirements for the channel or conduit are greatly reduced. Provides flexibility in the use of the collected water.
No retention	Channel or conduit is sized to convey peak flow with no retention of water.		Eliminates the need for runon retention structures and associated maintenance. More expensive than using an embankment for retention and controlled discharge of the peak flow.
Runoff collection System	Drained benches collect and remove precipitation falling on the disposal site.	Reduces erosion of fill and infiltration into fill. Collects water for reuse or discharge.	Decreases erosion and infiltration. Requires maintenance.
Runoff/leachate collection ponds	Lined ponds are used to retain leachate and runoff.	Prevents release of contaminated waters.	Collects water for reuse, treatment and discharge.

Source: EPA-600/8-83-003, 1983.

may include ditches, lined channels, conduits, and embankments arranged to direct the flow of surface water around or away from the waste material, and energy dissipators to moderate the impact of the flow.

The complexity and extent of the system will vary widely based on the amount of water to be diverted and the arrangement of the site. For a fill on a relatively level site, runon diversion may be only a system of channels and small embankments to deflect surface flow away from the landfill. In the case of a head-of-valley fill or a cross-valley fill, runon diversion might include an embankment dam to retain peak flows from the design storm until they can be passed through a conduit beneath or around the fill. Alternatively, the system may consist of a conduit or channel large enough to pass the design flow without an embankment (without retention).

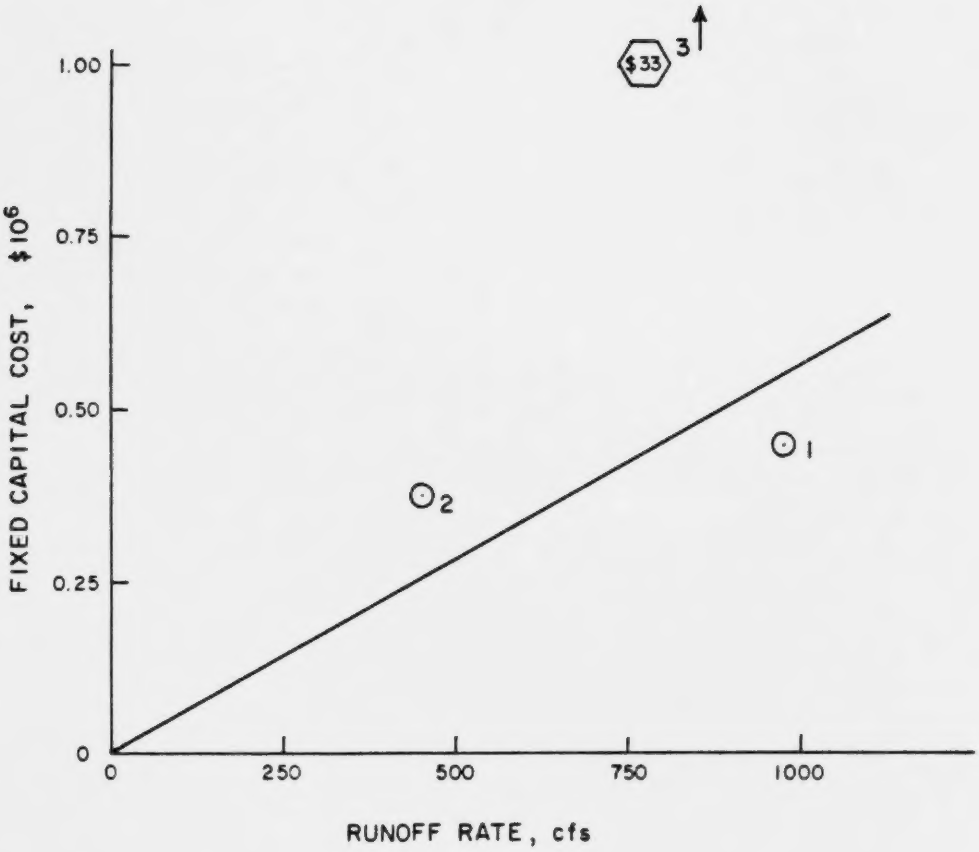
The costs for three runon diversion systems were estimated and they are plotted in Figure 4.3-2. Examples 1 and 2 consisted of runon retention in combination with continuous release. Example 3 was designed for no retention, which necessitated a large channel and extensive use of reinforced concrete energy dissipators; the higher cost associated with such a system is illustrated in the figure.

Examples 1 and 2 also consisted of an earth embankment for the retention of runon and an embedded conduit for controlled release. Channeling of the controlled release flow around the waste pile in Example 1 was accomplished with a lined canal, while Example 2 utilized an extension of the embedded conduit for the controlled release.

The cost of a runon diversion system will be influenced by: the size of the drainage area and topography which affect the runon rates, retentions, and embankment material quantities; the size, length, and complexity of controlled release structures and channeling systems; and the need for and extent of energy dissipators and/or drop structures. For example, the runon from a site with a large drainage area in a gently sloping topography could be diverted quite efficiently by an unlined canal or channel; another site with small runoff rates, but high erodible steep topography, may necessitate cost-intensive lined channels, flumes or conduits, as well as drop structures or energy dissipators. In summary, the cost of this sytem is highly site-specific.

Runoff Collection System

A runoff collection system usually consists of a system of channels, ditches, and conduits arranged to prevent the surface water that has contacted the waste material from leaving the site.



NOTES:

Examples 1 & 2 include retention with embankments and continuous controlled release through an embedded conduit.

Example 3 was designed to handle the maximum flow without retention.

Example 2 is specific to the TOSCO II case studies, except the embankment dam is smaller than the one proposed by Colony.

Mid 1980 $

Source: EPA-600/8-83-003, 1983

Figure 4.3-2. Runon Diversion Costs

Another purpose of this system is to drain the surface water from the wastes to limit the erosion and infiltration potential. Collected water may also be used to meet process needs.

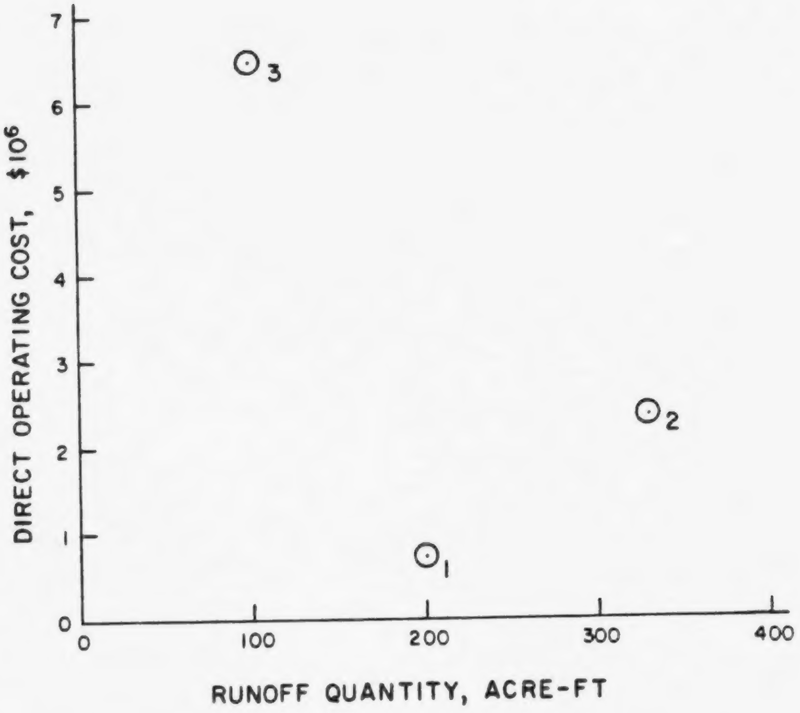
The basic elements of this system are backsloped benches on the face of the landfill and a means of collecting the water from the fill surface. Generally, half-round pipes, impervious membranes, or highly compacted soil or wastes are used to line ditches which collect the runoff from the bench and the segment of the landfill slope above it. The ditches then must be drained to a containment/ evaporation pond at the toe of the landfill, or the water must be impounded on the benches or top of the landfill. A problem with using embankments on the waste pile is that the water ponded on the landfill will have a greater tendency to infiltrate the waste material. This increased infiltration could have a detrimental effect on the stability of the slope and will somewhat increase the amount of water which must be handled by the leachate collection system (discussed under subsurface hydrology).

The costs for a variety of runoff collection system designs were estimated and these are plotted in Figure 4.3-3. Example 1 used shaped benches with unlined ditches for lateral conveyance and concrete weir collectors and corrugated metal pipe with energy dissipators for vertical conveyance. It also incorporated some temporary retention of runoff on the waste pile surface, which reduced the necessary capacity and cost of the vertical conveyance portion of the system. Example 2 used split corrugated metal pipe to line the collection ditches to facilitate lateral conveyance, and concrete weir collectors and corrugated metal pipe with energy dissipators for vertical conveyance. Example 3 used the lined ditches for lateral conveyance, with a concrete flume and a stilling basin for vertical conveyance.

The cost data, as can be seen in the plot, are highly dependent on the particular design, an no single cost curve relationship can be drawn through the data points. Example 1, which assumes a more modest design, defines the lower boundary of the cost envelope, and Example 3 defines the high end of the cost envelope.

Runoff/Leachate Collection Ponds

At the outlet of the collection system for surface runoff, a structure is needed to contain the collected water for reuse, treatment and discharge, or for evaporation. The structure would consist of an embankment across a former stream channel to form a pond, and the pond may be lined or unlined depending upon the nature of the impounded material. If a liner is needed, it would be protected from wave action, as necessary, using rip-rap, a sand layer, soil cement or similar materials. Since the pond would be located at the base of the landfill, it might also be used to collect the leachate from the fill.



NOTES:

Example 1 utilizes shaped benches as unlined ditches for lateral runoff conveyance.

Examples 2 & 3 utilize buried corrugated metal pipe to line ditches for lateral runoff conveyance.

Examples 1 & 2 utilize buried corrugated metal pipe and energy dissipators for vertical runoff conveyance.

Example 3 utilizes a concrete flume with stilling basin for vertical runoff conveyance.

Mid 1980 $

The costs indicated are cumulative for the project life.

Source: EPA-600/8-83-003, 1983

Figure 4.3-3. Runoff Collection Costs

Cost data for four examples of runoff/leachate collection ponds are presented in Figures 4.3-4 and 4.3-5. Figure 4.3-4 presents the total cost of the embankment and liner as a function of the construction material quantities used in each case, while Figure 4.3-5 isolates the cost of the liner as a function of the liner material quantity only.

Examples 1, 2 and 3 utilized compacted processed shale as a liner, while Example 4 used Mancos Shale as the liner. The relatively high cost of using an off-tract material (Example 4) is evident in the figures. The cost increase is incurred due to the source development, processing and hauling of Mancos Shale.

Slight cost differences may be observed between similar systems, and these can be attributed to site-specific features, such as the arrangement and configuration of the embankment and ponds.

4.3.2 Subsurface Hydrology Control Technologies

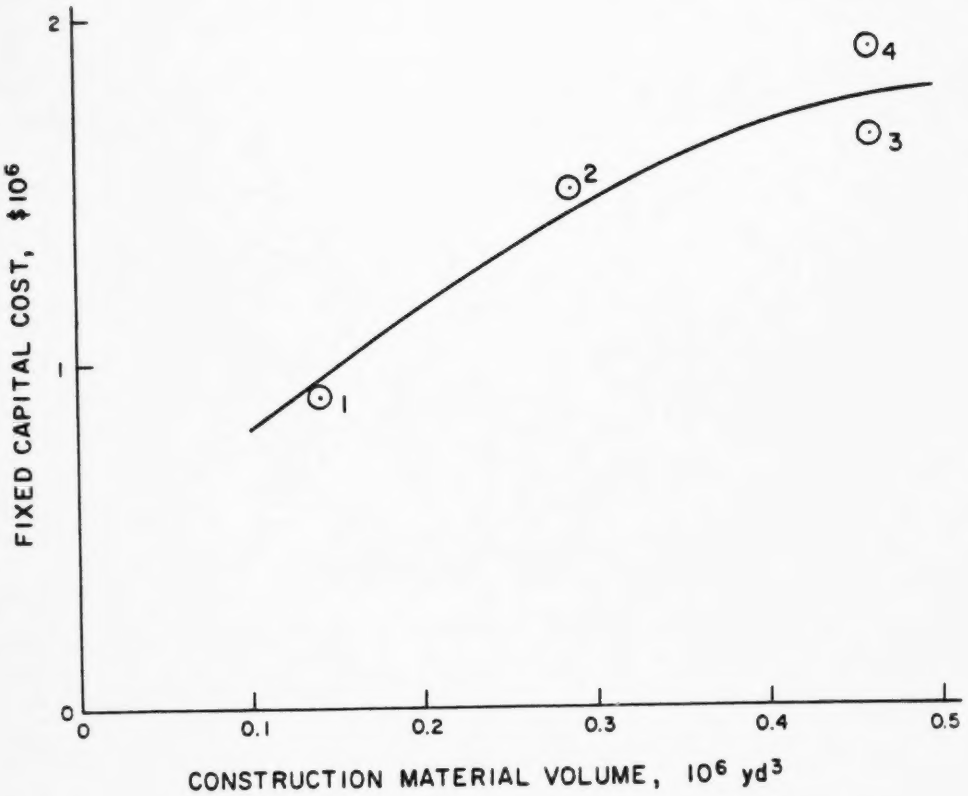
The technologies and practices in the area of subsurface hydrology involve the handling of groundwater seepage under a landfill to prevent infiltration of the pile and the control of water from the pile to prevent contamination of the groundwater.

The technologies, as summarized in Figure 4.3-6, are applicable to a surface landfill, and their key features are presented in Table 4.3-2. Detailed descriptions of the technologies, along with cost information, are presented below.

Liners and Covers

A liner is essentially a material with low water permeability that is installed at the bottom of a landfill or pond. Its purpose is to prevent the contaminated waters from the wastes from mixing with the groundwater. It also prevents groundwater from infiltrating the bottom of the landfill.

A cover is also made up of a low-permeability material and it is used as a surface sealer for the landfill. It prevents the runoff from infiltrating the pile, thereby reducing the quantity of the leachate and minimizing stability problems.



NOTES:

All Examples include cost of embankments and pond liners.

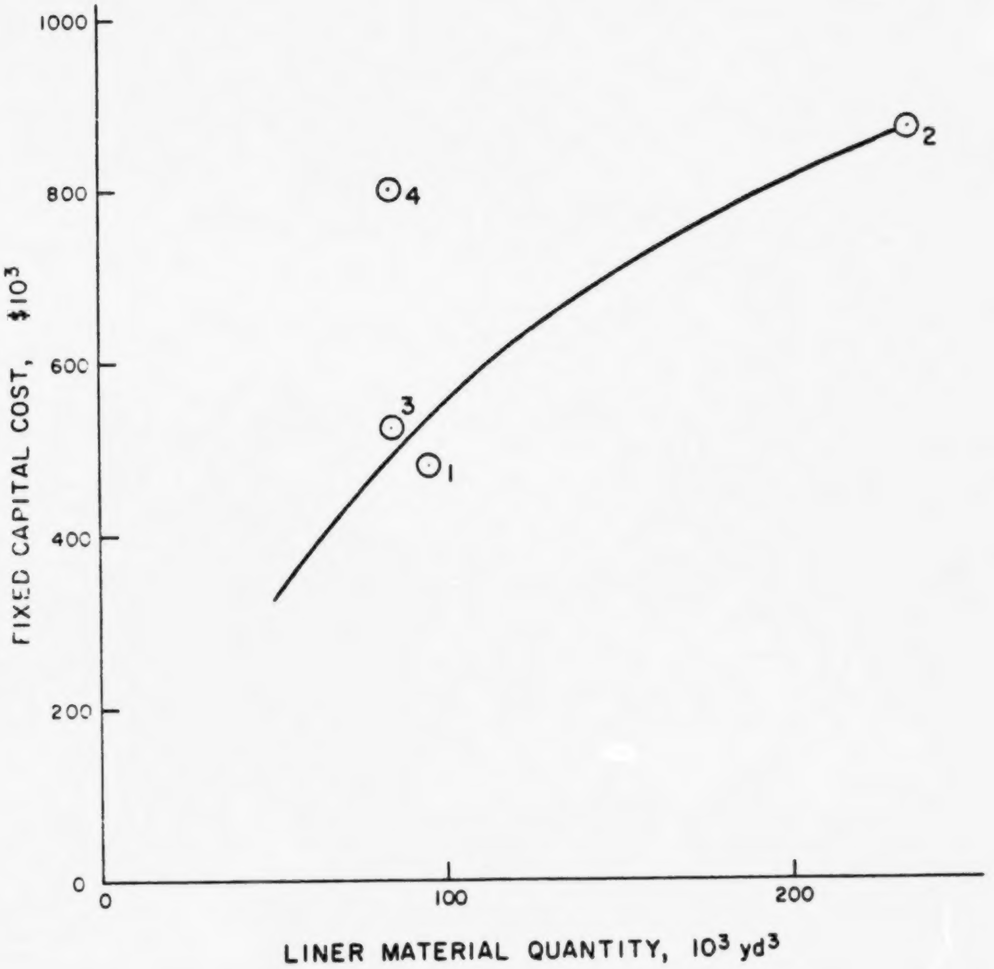
Examples 1,2 & 3 include pond liners constructed of processed shale.

Example 4 includes a liner constructed of Mancos Shale (off-tract material); cost is increased due to processing and transport.

Mid 1980 $

Source: EPA-600/8-83-003, 1983

Figure 4.3-4. Runoff/Leachate Pond Costs



NOTES:

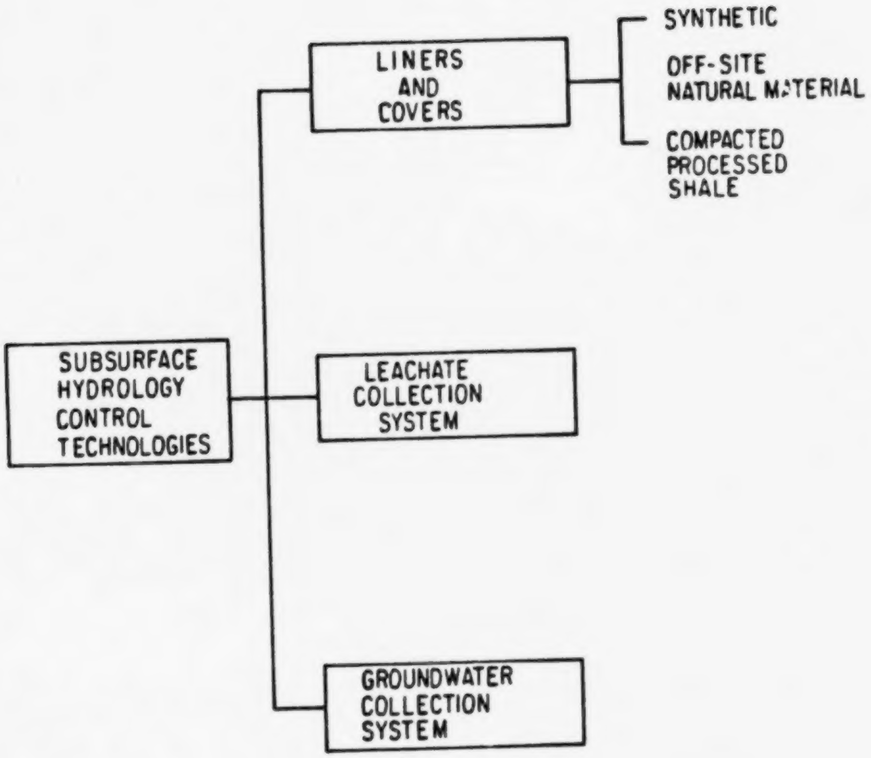
Examples 1, 2 & 3 include liners constructed of processed shale.

Example 4 includes a liner constructed of Mancos Shale (off-tract material); cost is increased due to processing and transport.

Mid 1980 $

Source: EPA-600/8-83-003, 1983

Figure 4.3-5. Runoff/Leachate Pond Liner Costs


SUBSURFACE HYDROLOGY CONTROL TECHNOLOGIES
LINERS AND COVERS
SYNTHETIC
OFF-SITE NATURAL MATERIAL
COMPACTED PROCESSED SHALE
LEACHATE COLLECTION SYSTEM
GROUNDWATER COLLECTION SYSTEM

Source: EPA-600/8-83-003, 1983

Figure 4.3-6. Subsurface Hydrology Control Technologies.

TABLE 4.3-2. KEY FEATURES OF SUBSURFACE HYDROLOGY CONTROL TECHNOLOGIES

Control technology	Principle	Purpose	Comments
Liners and covers	Low permeability layer severely restricts seepage.	Reduce formation of leachate. Prevent contamination of the groundwater by leachate from the fill. Prevent groundwater invasion of the fill, which might produce instability and additional leachate.	
Synthetic			Provide the lowest permeability but have the highest cost. Long-term durability is questionable.
Off-site natural material			High cost. Advantage is long-term durability.
Compacted processed shale			Lowest cost. Small particles may infiltrate adjacent drains. Advantage is long-term durability.
Leachate collection system	Collects leachate at the base of the landfill and drains into the pond.	Reduces groundwater contamination by effectively removing the leachate. Prevents loss of fill stability due to saturation.	Collected water may be used for process needs.
Groundwater collection system	Collects groundwater seepage beneath the landfill and drain.	Prevents loss of fill stability due to buildup of groundwater pressure beneath the liner.	Collected water may be used for process needs.

Source: EPA-600/8-83-003, 1983.

There are several materials which can be considered for the liners and covers. Probably the least expensive material would be compacted processed shale. It has the advantage of being readily available at the site. A similar lining could be made of processed shale or clay from off site if the quality of the processed shale from the site is unsuitable; however, these options would be relatively expensive due to the extra handling and hauling costs. There is also a variety of synthetic liners which could be considered. High-density polyethylene, for example, would range upward from a price similar to that for the off-site materials, depending upon the thickness used. This would make it very expensive for use in a processed shale landfill and it may have questionable long-term durability.

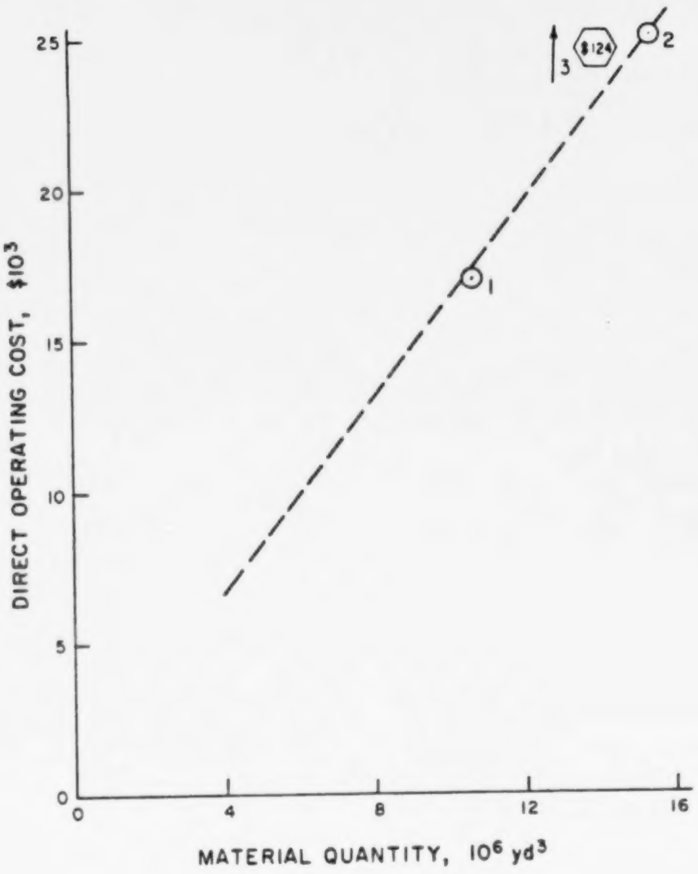
Linings made of natural or synthetic materials may dry and crack if they are left exposed to the weathering elements for long periods. The catchment and evaporation ponds presumably will need only one liner or no liner since they will not contain hazardous materials. If a combination of two liners is used, the synthetic liner may be placed above the natural material liner to prevent its drying and cracking. In cases where a synthetic liner is used, it should be covered by a layer of sand or gravel to protect it from traffic and wave action. Also, because of the weight of the fill and because the fill may be placed above an underground mine, the liner must accommodate a certain amount of subsidence and stretching and still function properly.

The cost of liners and covers depend on the quantity and type of material used. Figure 4.3-7 presents the costs for three separate liner and cover systems. Examples 1 and 2 assumed the use of highly compacted processed shale for construction of the liners, while Example 3 assumed the use of Mancos Shale. The compacted processed shale represents the lowest material cost option, while Mancos Shales is a more expensive natural material since it has associated source development, processing and hauling costs. The cost curve in the figure may be used to obtain an "order-of-magnitude" estimate of liner cost utilizing highly compacted processed shale as the construction material. The estimated cost for other liner materials would fall above this curve to a degree which is dependent on the source development, processing, and hauling costs associated with delivering these materials to the disposal site.

Leachate Collection System

The purpose of a leachate collection system is to collect water which infiltrates a landfill and drain it efficiently in order to prevent the saturation of the landfill and contamination of groundwater beneath the waste pile, as well as to facilitate handling of the leachate.

Leachate collection systems typically consist of blankets, or zones, of highly pervious sand and gravel. In some cases this is



NOTES:

Examples 1 & 2 utilize 3 feet of highly compacted processed shale for liner material.

Example 3 utilizes 3 feet of compacted Mancos Shale (off-tract material) for liner material; cost of processing and hauling this material makes this option more expensive than the others.

Mid 1980 $

Source: EPA-600/8-83-003, 1983

Figure 4.3-7. Liner Costs

augmented with embedded perforated pipe to increase the capacity, and it may also include collector ditches where the system emerges onto a broad level area. The sand or gravel layer would be located just above the bottom liner and it may be wrapped in filter fabric or surrounded by carefully graded sand filters to prevent infiltration by the processed shale particles. In either case, collection system should be designed so that movement and settlement do not result in discontinuity of the gravel layer or impede drainage to the collection or evaporation ponds.

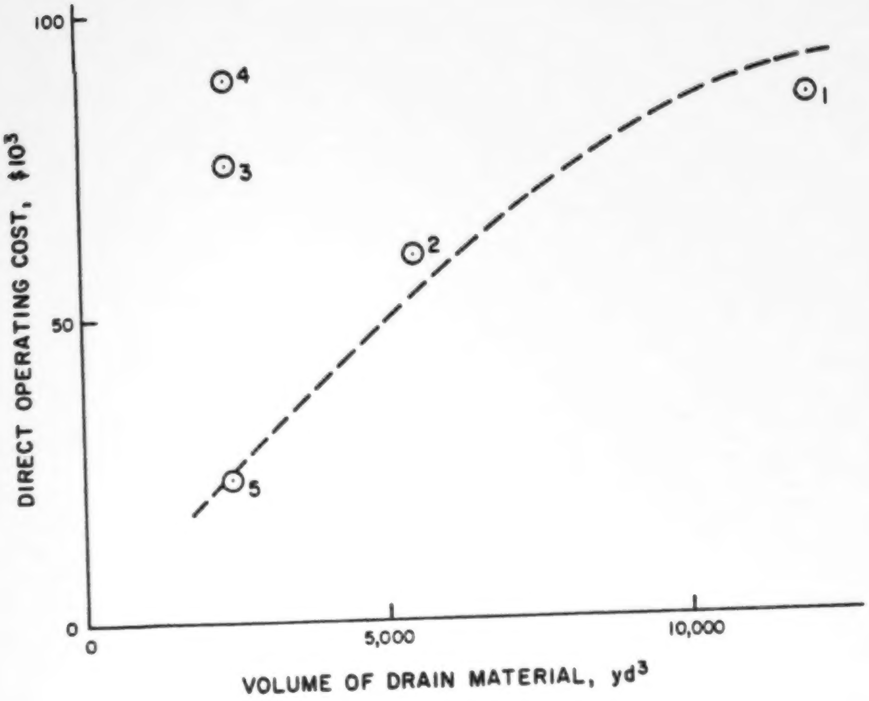
The costs for four distinct leachate collection systems were estimated and these are presented in Figure 4.3-8. In Examples 1 and 2, due to the valley shape of the disposal site, only the drain material was necessary for the collection system. The leachate in these two cases was drained in the runoff/leachate collection pond located downstream from the landfill. In Example 3, a toe ditch was necessary to collect the leachate due to the presence of the broad valley area at the toe of the landfill. The ditch was then drained into the common runoff/leachate collection pond. Example 4 also required a toe ditch which was drained into a leachate collection pond, while the runoff was impounded separately in evaporation ponds on the waste pile surface. Examples 3 and 4 required the same drainage material quantity. The cost difference between the two examples is due to the inclusion of a separate collection pond in Example 4. Data point 5 on the figure represents the cost of drainage material only for Examples 3 and 4. The cost of the toe ditch may be obtained by subtracting data point 5 from 4.

The costs for similar systems should be proportional to the volume of drainage material used, but slight deviations may be encountered due to the site-specific conditions.

Groundwater Collection System

The purpose of a groundwater collection system is to relieve pressure from the seeps and springs beneath a landfill. This situation is most likely in the cases of cross-valley or head-of valley landfills. The system will be essentially identical to the leachate collection system except it would be below the bottom liner rather than above it.

Groundwater collection systems typically consist of blankets or zones of pervious sand and gravel drained beyond the perimeter of the landfill. This may be augmented with embedded perforated pipe to increase capacity and with collector ditches. The sand or gravel layer would be lined as necessary with filter fabric or surrounded by properly graded sand filters to prevent infiltration of smaller particles from adjacent materials. The system must also be designed to maintain its continuity despite possible subsidence or settlement of the landfill.



NOTES:

Examples 1 & 2 require only drain material due to the valley shape; leachate containment is performed by the contaminated runoff catchment pond of which the leachate is a negligible component.

Example 3 includes cost of toe ditch for collection due to broad valley at waste pile toe; containment is also by the contaminated runoff catchment pond.

Example 4 includes toe ditch collection and separate containment pond because, in this case, contaminated runoff is contained in evaporation ponds on the waste pile surface.

Example 5 includes only the drain material cost of Examples 3 & 4.

Mid 1980 $

The costs indicated are cumulative for the project like.

Source: EPA-600/8-83-003, 1983

Figure 4.3-8. Leachate Collection Costs

The costs of two groundwater collection systems were estimated and these are plotted in Figure 4.3-9. Both systems used gravel blankets under the pile to collect the groundwater seepage. In Example 2 the gravel blankets were used only above the seeps and springs, while in Example 1 an extensive network of the blankets was considered, resulting in a higher cost. The cost of the collection system should be proportional to the quantity of the drainage material used.

4.3.3 Surface Stabilization Technologies

The activities and technologies in the area of surface stabilization involve the treatment of the disturbed land surface and the problems associated with the disposal and reclamation of the waste material. These technologies are outlined in Figure 4.3-10 and their key features are presented in Table 4.3-3.

Dust Control

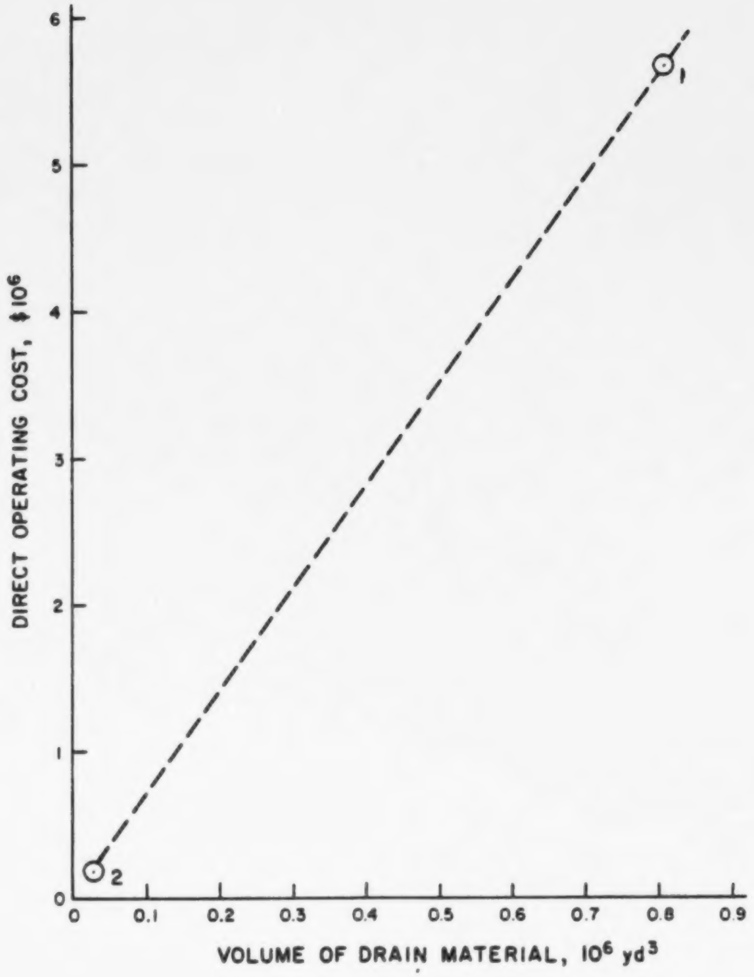
The purpose of dust suppression is to limit pollution from airborne dust, particularly during the placement of the waste material in a fill. Dust suppression can be accomplished by spraying the haul roads and fill surface with water or a combination of water and a chemical binder. Haul roads could, alternatively, be paved.

Use of water along for dust suppression would necessitate repeated applications, often more than one per day, to be effective. Water with a chemical binder should necessitate only a few applications to a given surface to stabilize it for a year or more unless it receives heavy traffic. Finally, vegetation would provide perhaps the most permanent means of dust control, but this would not be practical except on surfaces which would not be disturbed for a number of years.

The dust suppression technology assumed in developing the cost data for two examples consisted of routine spraying of the processed shale pile with water and additives to minimize the dust generated due to the wind and the waste hauling and placement activities. Depending on the processed shale characteristics, this operation could either be continuous or intermittent. The cost curve in Figure 4.3-11 is based on the assumption that both the manpower and equipment operation requirements are continuous. Theoretically, these requirements could differ depending on the rate of waste production and the surface area of the particular waste pile; however, both cases estimated were assumed to be equivalent in this respect.

Erosion Control

The purpose of erosion control is to keep the waste material in place so that the surface drains remain free flowing, the slopes



NOTES:

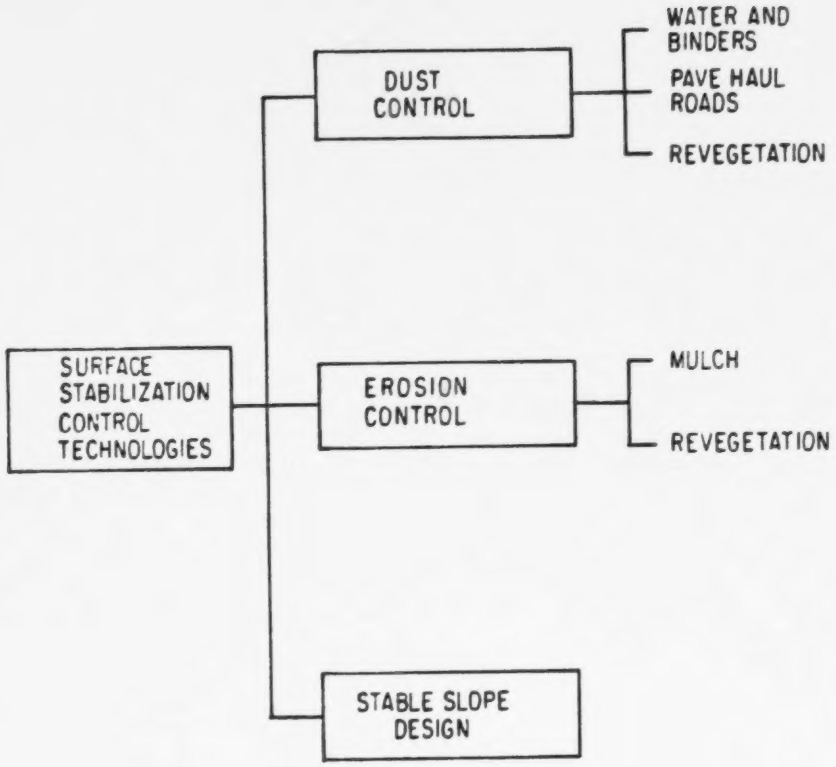
Examples 1 & 2 consist of gravel blankets for collection of groundwater from springs and seeps; extent of blankets dictated by the existence and extent of such conditions.

Mid 1980 $

The costs indicated are cumulative for the project life.

Source: EPA-600/8-83-003, 1983

Figure 4.3-9. Groundwater Collection Costs


SURFACE STABILIZATION CONTROL TECHNOLOGIES
DUST CONTROL
WATER AND BINDERS
PAVE HAUL ROADS
REVEGETATION
EROSION CONTROL
MULCH
REVEGETATION
STABLE SLOPE DESIGN

Source: EPA-600/8-83-003, 1983

Figure 4.3-10. Surface Stabilization Technologies

TABLE 4.3-3. KEY FEATURES OF SURFACE STABILIZATION TECHNOLOGIES

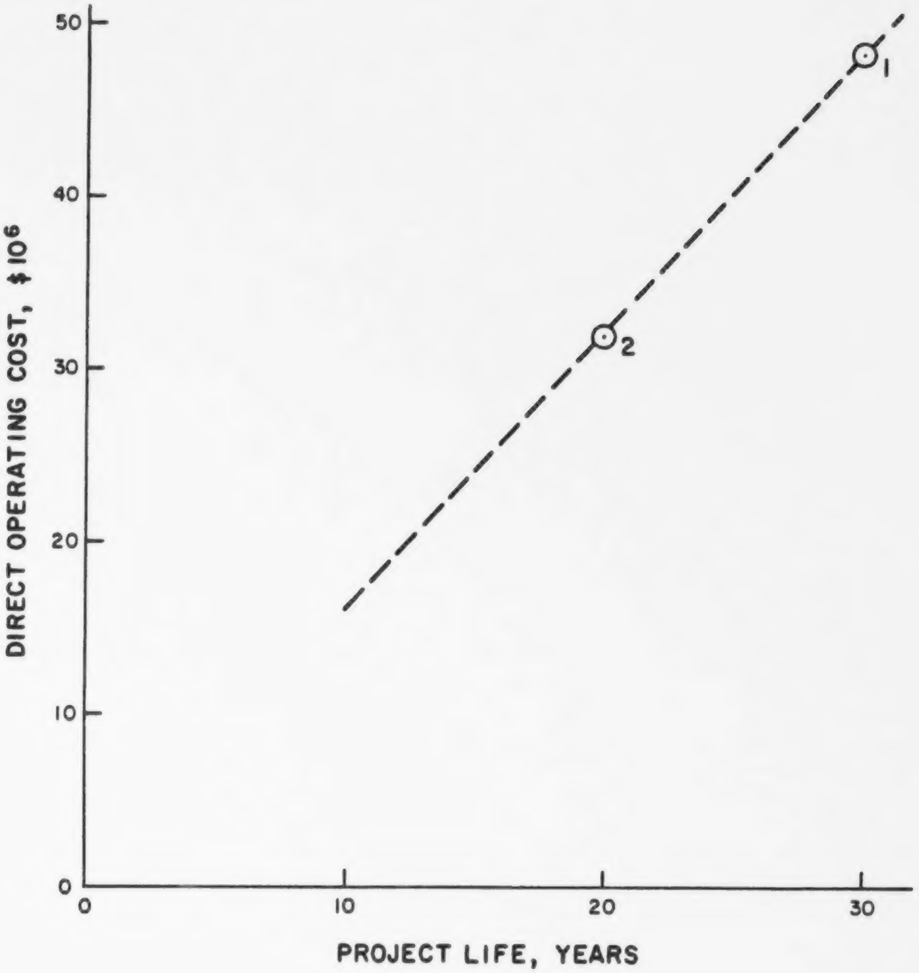
Control technology	Principle	Purpose	Comments
Dust control		Prevents or limits dust pollution from wind blowing across exposed surfaces or from vehicular traffic.	
Water and binders	Fluid sprayed on the surface binds the fine particles together.		Well developed technology that is commonly used in mining operations.
Pave haul roads	A hard surface on the haul road prevents generation of dust by vehicular traffic.		Should improve traffic conditions on the road.
Revegetation	Vegetation prevents dust caused by wind.		Not useful in areas with any equipment traffic or where the surface is being disturbed by other activities.

(continued)

TABLE 4.3-3 (continued)

Control technology	Principle	Purpose	Comments
Erosion control		Simplifies reclamation, prevents blockage of the drains, and prevents contamination of surface waters by eroded material.	
Mulch	Various materials are placed on the slope to limit erosion.		Quick and easy to accomplish but is only a temporary measure.
Revegetation	Plant growth is started on the slope to limit erosion.		Permanent control but slow to achieve.
Stable slope design	Design slope to minimize stability problems and maintenance.	Makes erosion control, revegetation, and drainage easier. Restricts waste material to a definite, predefined area.	

Source: EPA-600/8-83-003, 1983.



NOTES:

Example 1 assumes a 30-year project life, while Example 2 assumes a 20-year life.

Mid 1980 $

The costs indicated are cumulative for the project life.

Source: EPA-600/8-83-003, 1983

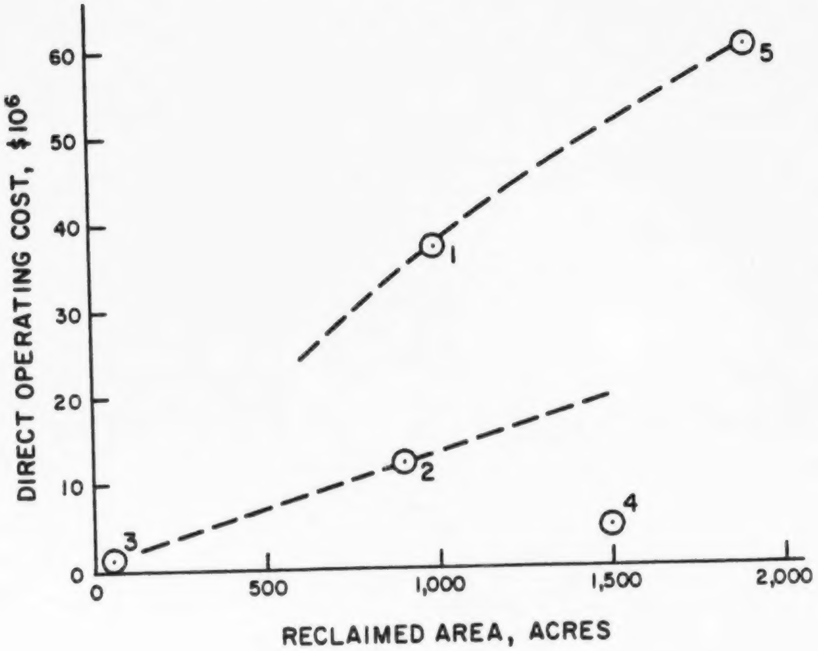
Figure 4.3-11. Dust Control Costs

remain stable, eroded material does not pollute surface streams, and reclamation and revegetation efforts are not hampered. Some means of limiting erosion include contouring the surface with short and gentle slopes, providing for drainage of the slopes at frequent intervals, using mulch or filter fabric to dampen the impact of water flow, and revegetating the completed faces. Of these measures, grading and drainage are essential, take effect immediately, and last as long as they are maintained. Mulch or filter fabric also provide a quick control, but they are of a temporary nature. Revegetation provides a permanent control, but it is generally slower to take effect.

A major consideration in planning erosion control measures is the severity of rainfall in the area. A large proportion of the water from a high-intensity rainfall would run off the surface, thus increasing the erosion.

Reclamation and revegetation consist of placing a subsoil and topsoil strata of sufficient thickness to support vegetation, and then seeding the disposal area with native or introduced species. The greatest contributor to the magnitude of cost for this control technology is the thickness of the soil strata and the costs associated with the delivered soil material, i.e., the source development, processing and hauling costs. Soil and subsoil stripped from the disposal site may not be available in sufficient quantity to meet the reclamation needs. The cost curves presented in Figure 4.3-12 illustrate five examples. Examples 1 and 5 included 2 feet of subsoil (sand-gravel material) and 30 inches of topsoil, both of which were brought in from off-site sources and thus had additional costs involved. Examples 2 and 3 also used the same thicknesses, but the soils were available on the site. Example 4 used no subsoil and only 6 inches of topsoil which was available on the site; therefore, additional material costs were not involved. All examples included the cost of revegetation. It is evident from the figure that the cost of erosion control can vary significantly depending on the factors considered; however, in any category, the costs are proportional to the area reclaimed and revegetated.

Besides improving the appearance of the landscape, the vegetation of the waste landfill will serve other purposes that are important from the pollution control point of view. The physical effect of wind and water will be greatly influenced by the presence of vegetation on the surface. Dense vegetation and root systems will reduce the weathering impacts, thereby reducing the erosion by wind and precipitation run-off. The vegetation will aid in evapotranspiration of the surface-absorbed water thereby reducing water infiltration and leaching. Vegetation will also provide a suitable environment for other biological activity which will aid in restoring the local ecosystem.



NOTES:

Examples 1 & 5 include 2 feet of subsoil and 30 inches of topsoil, both obtained off site.

Examples 2 & 3 include 2 feet of subsoil and 30 inches of topsoil obtained on site.

Example 4 includes no subsoil and only 6 inches of topsoil obtained on site.

Mid 1980 $

The costs indicated are cumulative for the project life.

Source: EPA-600/8-83-003, 1983

Figure 4.3-12. Reclamation and Revegetation Costs

The use of the processed shale itself as a plant growth medium may be questionable. The texture, salinity, alkalinity, color, etc, of the processed shales play an important role in the growth of vegetation. Some type of modification in the processed shale properties and/or application of a natural soil cover may be necessary to induce and sustain vegetation on the processed shale.

If the top layers of the processed shales are thoroughly leached so that the salinity is within acceptable range, the planting or seed germination may be possible in the processed shale itself. Otherwise topsoil may need to be placed on the shale waste, or a mixture of rock, topsoil and subsoil can be mixed into the top layers. Topsoil in the oil shale area is usually insufficient to provide a good cover; therefore, mixing with rocks and subsoils may be necessary to give proper depth. Also, a proper selection of the plant species that would survive the climate of the region and high salt concentration of the processed shale should be made. Soil fertilization should be carried out to make up for the nutrient deficiency, and sufficient water should be made available while establishing the vegetation.

Stable Slope Design

The purpose of designing the slopes to be stable under prevailing conditions is to minimize the maintenance of the landfill and to avoid hampering of the reclamation and revegetation efforts. The techniques used in designing stable slopes are a well developed part of soils engineering. To arrive at the most advantageous slope design, other factors besides basic stability, such as erosion, ease of placement, reclamation and revegetation, must be considered. However, the physical characteristics of the waste material will dictate a limiting slope angle. The costs of achieving a stable slope design are incidental to the placement and revegetation of the fill material; hence, additional costs are not involved.

4.3.4 Summary of Control Technologies

Table 4.3-4 presents a summary of the control technologies and estimated costs (1980 dollars) for disposal of retorted shale from a small (47,000 bbl/day) oil shale plant. Not included are the costs for offsite disposal of hazardous wastes. Also excluded are the considerable costs for transporting the retorted shale to the disposal site and compacting it in lifts which would have to be done for process reasons rather than environmental control.

TABLE 4.3-4. ENGINEERING COSTS AND TIMING OF SOLID WASTE MANAGEMENT ACTIVITIES FOR A 47,000 bbl/day FACILITY[a] (Thousands of Dollars)

Activity	Project year							
	0	1[b]	2	3	4	5	6	7
Surface hydrology								
Runoff collection			162	162	162	162	162	162
Surface cover			564	564	564	564	564	564
Upper embankment		209						
Lower embankment		304	304	304				
Runon diversion		261						
Stilling basins		2	2	2	2	2	2	2
Water impoundments		1,338	1,338	1,338				
Subsurface hydrology								
Bottom liner		594	594	594	594	594	594	594
Shale underdrain		4	4	4	4	4	4	4
Monitoring wells	83							
Groundwater collection	6	12	12	12	12	12	12	12
Surface stabilization								
Clear and grub	62	62	62	62	62	62	62	62
Strip topsoil	289	289	289	289	289	289	289	289
Dust suppression		1,615	1,615	1,615	1,615	1,615	1,615	1,615
Reclamation and revegetation			60	120	120	120	120	120
TOTAL (all items)	440	4,690	5,006	5,066	3,424	3,424	3,424	3,424

(continued)

TABLE 4.3-4 (continued)

Activity	Project year 8	9	10	11	12	13	14	15
Surface hydrology								
Runoff collection	162	162	162	162	162	162	162	162
Surface cover	564	564	564	564	564	564	564	564
Upper embankment								
Lower embankment								
Runon diversion								
Stilling basins	2	2	2	2	2	2	2	2
Water impoundments								
Subsurface hydrology								
Bottom liner	594	594	594	594	594	594	594	594
Shale underdrain	4	4	4	4	4	4	4	4
Monitoring wells			17					
Groundwater collection	12	12	12	12	12	12	12	
Surface stabilization								
Clear and grub	62	62	62	62	62	62	62	62
Strip topsoil	289	289	289	289	289	289	289	289
Dust suppression	1,615	1,615	1,615	1,615	1,615	1,615	1,615	1,615
Reclamation and revegetation	120	120	120	120	120	120	120	120
TOTAL (all items)	3,424	3,424	3,441	3,424	3,424	3,424	3,424	3,412

(continued)

TABLE 4.3-4 (continued)

Activity	Project year 16	17	18	19	20	21
Surface hydrology						
Runoff collection	162	162	162	162	162	162
Surface cover	564	564	564	564	564	564
Upper embankment						
Lower embankment						
Runon diversion						
Stilling basins	2	2				
Water impoundments						
Subsurface hydrology						
Bottom liner	594	594	594	594		
Shale underdrain	4	4	4	4		
Monitoring wells				17		
Groundwater collection						
Surface stabilization						
Clear and grub	62	62	62	31		
Strip topsoil	289	289	289	144		
Dust suppression	1,615	1,615	1,615	1,615	1,615	
Reclamation and revegetation	120	120	120	120	120	120
TOTAL (all items)	3,412	3,412	3,410	3,251	2,461	846

[a] Mid 1980 $

[b] Year 1 is the first year of production.
Source: EPA-600/8-83-003, 1983.

REFERENCES

Agapito, J. Pillar Design in Competent Bedded Formations. Thesis 1485, Graduate School, Colorado School of Mines, 1972.

Allen, R. R., and Parry, V. F. U.S. Bureau of Mines. Storage of Low Rank Coals, Report of Investigation No. 5034, 1954.

Ash, H. O. Guidebook to the Energy Resources of the Piceance Creek Basin, Colorado. Federal Oil Shale Leasing and Administration, U.S. Department of the Interior, Denver, Colorado, 1974.

Bates, E. R. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268. Based on Multiple Sources. January 1985.

Bates, T. F., and E. O. Strohl. Minerology, Petrography, and Radioactivity of Representative Samples of Chattanooga Shale. Bulletin of the Geological Society of America, Vol. 68, 1957.

Battelle, Pacific Northwest Laboratory. PNL-3830, Vol. 1, Main Report. Western Oil Shale Development: A Technology Assessment. November 1981. Prepared for the U.S. Department of Energy under contract DE-AC06-76RLO-1830.

Baughman, G. L. Synthetic Fuels Data Handbook. Cameron Engineer's Inc. (A Division of The Pace Company Consultants and Engineers, Inc.) Second Edition, 1978.

Bouchta, Rabah, Said Berrada, Chang Yul Cha, and U-Sun Park. Development of T^3 - Process in Morocco. 6th IIASA Resources Conference on World Oil Shale Resources and Their Potential Development, Golden, Colorado, June 14-19, 1981.

Bradley, W. H. Origin and Microfossils of the Oil Shale of the Green River Formation of Colorado and Utah, USGS Professional Paper, 168, 1931.

Brown, A., et al. Water Management in Oil Shale Mining. Golder Assoc., Inc. U.S. Bureau of Mines, Contract No. J0265019, September 1977.

Bureau of Land Management. U.S. Department of the Interior, Grand Junction, Colorado 81501. Final Environmental Impact Statement, Clear Creek Shale Oil Project, 30 September 1983.

Bureau of Land Management. U.S. Department of the Interior, Utah State Office, Salt Lake City, Utah 84111. Final Environmental Impact Statement on the Uintah Basin Synfuels Development. February 1983.

Cashion, W. B. Geology and Fuel Resources of the Green River Formation, Southeastern Uinta Basin, Utah and Colorado. USGS Professional Paper 548, 1967.

Cashion, W. B., and J. R. Donnell. Revision of Nomenclature of the Upper Part of the Green River Formation, Piceance Creek Basin, Colorado, and Eastern Basins, Utah, 1974.

Chevron Research Company, Richmond, California 94802. Chevron Research Company Temporary Shale Oil Semi-Works Development Facility Solid Waste Disposal Permit Application. Prepared by Morrison-Knudsen Company, Inc., Boise, Idaho 83729. Submitted to Utah Bureau of Solid Waste Management, May 1981.

Conant, L. C., and V. E. Swanson. Chattanooga Shale and Related Rocks of Central Tennessee and Nearby Areas. U.S. Geological Survey Professional Paper 357, 1961.

Culbertson, W. C. Geology and Mineral Resources of the Green River Formation, Wyoming. Presented at the United Nations Symposium on the Development and Utilizaiton of Oil Shale Resources, Tallinn, U.S.S.R., 1968.

Culbertson, W. C. Trona in the Wilkens Peak Member of the Green River Formation, SW, Wyoming. USGS Professional Paper 550B.

Culbertson, W. C., and J. K. Pitman. Oil Shale, U.S. Mineral Resources. Professional Paper No. 820, U.S. Geological Survey, Denver, Colorado, 1973.

Davis, E. C., and W. J. Boegly, Jr. A Review of the literature on leachates from coal storage piles. Oak Ridge National Laboratory Report No. ORNL/TM-6186, January 1978.

Denver Research Institute, University of Denver, Denver, Colorado 80208. Systems Applications Inc., San Rafael, California 94903. Kaman Sciences Corporation, Kaman Tempo, Santa Barbara, California 93102. Draft Report: Overview of the Environmental Problems of Oil Shale Development. Prepared under Contract 68-03-2795. Project Officer: R. C. Thurnau, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

Denver Research Institute, University of Denver, Denver, Colorado 80208. Draft Report DRI No. 5269. Characterization of Contaminants in Oil Shale Residuals and the Potential for Their Management to Meet Environmental Quality Standards. Second and Third Annual Report, NSF (RANN) Grant No. ENV75-00175-A02. J. J. Schmidt-Collerus, Principal Investigator. April 1980.

Denver Research Institute, University of Denver, Denver, Colorado 80208. Trace Elements Associated with Oil Shale and Its Processing. Prepared for The Environmental Protection Agency, Industrial Environmental Research Laboratory, under contract 68-02-1881, May 1977.

Denver Research Institute, University of Denver, Denver, Colorado 80208. An Engineering Analysis Report on the Paraho Oil Shale Process, C. H. Prien. Prepared for Industrial Environmental Research Laboratory, USEPA, Cincinnati, Ohio 45268; under EPA contract No. 68-02-1881; Project Officer T. J. Powers III. 24 June 1977.

Dinneen, G. V., and others. Constitution of Green River Oil Shale. Presented at the U.N. Symposium on the Development and Utilization of Oil Shale Resources, Tallinn, U.S.S.R., 1968.

Dinneen, G. V. Oil Shale and the Energy Crisis. American Society of Mechanical Engineers, 1972 Winter Meeting, New York, N.Y., 1972.

DOE/EV-0078, May 1980. Environmental Research on a Modified *In Situ* Oil Shale Process: A Progress Report from the Oil Shale Task Force. U.S. Department of Energy, Washington, DC 20545.

DOE/EV-86, June 1980. Paraho Environmental Data. Part I: Process Characterization; Part II: Air Quality; Part III Water Quality. Prepared by R. N. Heistand, R. A. Atwood and K. L. Richardson. Prepared for U.S. Department of Energy, Washington, DC 20858.

DOE/FE/60177-1590 (DE84012285), April 1984. Postburn Characterization of a Geokinetics *In Situ* Oil Shale Retort. G. M. Mason, R. D. Giauque and D. B. McWhorter. Work performed under Interagency Agreement AD-89-F-0-026-0 and Cooperative Agreement DE-FC21-83FE60177 for U.S. Department of Energy by Western Research Institute, Laramie, Wyoming.

Donnell, J. R. Tertiary Geology and Oil Shale Resources of the Piceance Creek Basin, NW Colorado. USGS Bulletin 1082-L, 1961.

Donnell, J. R. Mercury in Oil Shale From the Mahogany Zone of the Green River Formation. USGS, Journal of Research, Vol. 5, No. 2, March-April 1977.

Dravo Corporation. Materials Handling Techniques for Backfilling Proposed Oil Shale Mines. 1975.

Duncan, D. C. and V. E. Swanson. Organic Rich Shales of the U.S. and World Land Areas. U.S. Circular 523, U.S. Geological Survey, Denver, Colorado, 1965.

Engineering-Science, Inc., Denver, Colorado 80212. Draft Summary Report: Hazard Assessment of Pollutant Emissions from Shale Oil Production Facilities. Prepared for USEPA Region VIII, June 1983.

EPA-600/7-79-075, March 1979. Technological Overview Reports for Eight Shale Oil Recovery Processes. C. C. Shih, J. E. Cotter, C. H. Prien and T. D. Nevens, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA 600/7-80-181, 1980. Reconnaissance Study of Leachate Quality From Raw-Mined Oil Shale-Laboratory Columns. D. B. McWhorter, Colorado State University. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA-600/2-80-205a, 1980. Environmental Perspective on the Emerging Oil Shale Industry. EPA Oil Shale Research Group. E. R. Bates and T. L. Thoem, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA-600/8-83-003, April 1983. Pollution Control Technical Manual: TOSCO II Oil Shale Retorting with Underground Mining. Denver Research Institute. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA-600/8-83-004, April 1983. Pollution Control Technical Manual: Modified *In Situ* Oil Shale Retorting. Denver Research Institute. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA-600/8-83-005, April 1983. Pollution Control Technical Manual: Lurgi Oil Shale Retorting with Open Pit Mining. Denver Research Institute. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA-600/2-84-153, 1984. Auto-oxidation Potential of Raw and Retorted Oil Shale. A. D. Green, Research Triangle Institute. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA-600/D-84-036, March 1984. Environmental Research Brief, Oil Shale Potential Environmental Impacts and Control Technology. E. R. Bates, W. W. Liberick, J. Burckle, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA-600/D-84-228, 1984. Leaching Characteristics and Hydraulic Properties of Retorted Oil Shales. D. B. McWhorter, Colorado State University. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

EPA 600/D-84-143, August 1984. Environmental Research Brief. Quality and Quantity of Leachate from Raw Mined Colorado Oil Shale. D. B. McWhorter, Colorado State University. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

Fahey, J. J. Saline Minerals of the Green River Formation. USGS Professional Paper 405, 1962.

Faulkner, B. P., M. H. Weinecke and R. F. Cnare. Results of the Processing of a Western Oil on the Allis-Chalmers Roller Grate Retort System. Sixteenth Oil Shale Symposium, April 13-15, 1983; Proceedings published by Colorado School of Mines Press, (Editor: J. H. Gary), August 1983.

Forbes, F. and F. W. Kinsey. The Dravo Traveling Grate Process for Oil Shale Retorting. Proceedings, 1981 Eastern Oil Shale Symposium, November 15-17, 1981, Lexington, KY. Proceedings published by Institute for Mining & Mineral Research, Lexington, KY 40512.

Fox, J. P. Leaching of Oil Shale Solid Wastes: A Critical Review. July 1983. Prepared for the Center for Environmental Sciences, University of Colorado at Denver, Denver, CO 80202. Work supported by U.S. Department of Energy under Contract Numbers DE-AC02-79-EV10298 and DE-AC03-76SF00098.

Guney, M., and D. J. Hodges. Adiabatic Studies of Spontaneous Heating of Coal, Part I. Coll. Guard., V. 217, No. 2, 1969, pp. 105-109.

Heistand, R. N., 8185 E. Geddes Ave., Englewood, CO 80112. Private Communication, September 1984.

Hite, R. J., and J. W. Dyni. Potential Resources of Dawsonite and Nahcolite in the Piceance Creek Basin, NW Colorado. Quarterly of the Colorado School of Mines, Vol. 62, No. 3, 1967, pp. 591-604.

Herron, J. T., W. A. Berg and H. P. Harbert III. Vegetation and Lysimeter Studies on Decarbonized Oil Shale. Colorado State University Experiment Station, Fort Collins, Colorado 80523, Technical Bulletin 136, January 1980.

Holtz, W. G. Woodward-Clyde Consultants. Disposal of Retorted Oil Shale from the Paraho Oil Shale Project. USBM Contract JO255004. December 1976.

Jackson, L. P. and K. F. Jackson. The Co-disposal of Retorted Shale and Process Waters: Effect on Shale Leachate Composition. Fifteenth Oil Shale Symposium, April 28-30, 1982, Golden, Colorado. Proceedings (J. H. Gary, Editor) published by Colorado School of Mines Press, August 1982.

Kim, A. G. Laboratory studies on spontaneous heating of coal: A summary of Information in the Literature. U.S. Dept. of the Interior, Bureau of Mines, IC8756, 1977.

Lowry, H. H. Chemistry of Coal Utilization, Vol. 1, John Wiley & Sons, 1954.

Margheim, G. A. Water Pollution from Spent Oil Shale. Ph. D. Dissertation, Colorado State University, Fort Collins, CO, May 1975.

Matzick, A., and others. Development of the USBM Gas Combustion Oil Shale Retorting Process. USBM Bulletin 635, 1966.

Monsanto Company, 1515 Nicholas Road, Dayton, Ohio 45418. Duane Day, Personal Communication, February 1984.

Monsanto Company, 1515 Nicholas Road, Dayton, Ohio 45418. A. K. Agarwal, August 1984. Based on TRW, March 1977.

Murray, D. K., and J. D. Haun. Introduction to the Geology of the Piceance Creek Basin and Vicinity, Northwestern Colorado. Rocky Mountain Association of Geologists, Guidebook, 1974.

Paraho Development Corporation, June 1982. Paraho-Ute Project Technical Report. Requested by the Bureau of Land Management EIS Services, Denver, CO.

Poulson, R. E., and others. Minor Elements in Oil Shale and Oil Shale Products. Presented at the NBS/EPA Workshop on Standard Reference Materials for Oil Shale Environmental Concerns, Gaithersburg, Maryland, November 1975.

Roehler, H. W. Depositional Environments of Rocks in the Piceance Creek Basin, Colorado, Rocky Mountain Association of Geologists. Guidebook to the Energy Resources of the Piceance Creek Basin, Colorado, 1974.

Roehler, H. W. Mineral Resources in the Washakie Basin, Wyoming and Sand Wash Basin, Colorado. Wyoming Geological Association Guidebook, Greater Green River Basin Symposium, 1973.

Schemling, W. A. et al. Spontaneous Combustion Liability of Subbituminous Coals: Development of a Simplified Test Method for Field Lab/Mine Application. Analytic Chemistry of Liquid Fuel Sources, P. C. Uden et al., eds, ACS 1978.

Schuman, G. E., W. A. Berg and J. F. Power. Management of Mine Wastes in the Western United States, Land Applications of Waste Materials. Published in 1976 by Soil Conservation Society of America, Ankeny, Iowa.

Sellers, J. B. Rock Mechanics Research in Oil Shale Mining. 100th National Meeting of AIME, New York, N.Y., 1971.

Smith, J. W. Specific Gravity - Oil Yield Relationships of Two Colorado Oil Shale Cores, Industrial and Engineering Chemistry, Vol. 48, No. 3, 1956, pp. 441-44.

Smith, J. W. Ultimate Composition of Organic Material in Green River Oil Shale. U.S. Bureau of Mines Report of Investigations No. 5725, 1961.

Smith, J. W. Stratigraphic Change in Organic Composition Demonstrated by Oil Specific Gravity-Depth Correlation in Green River Oil Shale. AAPG Bulletin, Vol. 47, No. 5, May 1963.

Smith, J. W., and N. B. Young. Specific Gravity to Oil Yield Relationships for Black Shales of Kentucky's New Albany Formulation. USBM Report of Investigations No. 6531, 1964.

Smith, J. W., and N. B. Young. Organic Composition of Kentucky's New Albany Shale; Determination and Uses. Elsevier Publishing Company, Amsterdam, 1967.

Smith, J. W. Simultaneous DTA-TG-MSA Apparatus for Thermal Study of Natural Fuels, International Conference on Thermal Analysis, 1968.

Smith, J. W. Theoretical Relationship Between Density and Oil Yield for Oil Shales. USBM Report of Investigations 7248, 1969.

Smith, J. W., W. A. Robb, and N. B. Young. High Temperature Reactions of Oil Shale Minerals and Their Benefit to Oil Shale Processing in Place. Presented at the 11th Oil Shale Symposium, Colorado School of Mines, Golden, Colorado, 1978.

Stanfield, K. E. Properties of Colorado Oil Shale. USBM Report of Investigations 4825, 1951.

Stollenwerk, K. G. and D. D. Runnells. Env. Sc. & Technol., November 1981, pp. 1340-1346.

Taback, H. J., G. C. Quartucy and R. J. Goldstick. KVB, Inc., Engineering and Research Division, Irvine, CA 92714. Test of a Stretford Plant and an Alkaline Scrubber on Gases from an Oil Shale *In Situ* Retort at Geokinetics, Inc., Uintah County, Utah. KVB-807430-1982. Prepared for USEPA. Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268. August 1984.

Tamm, P. W., C. A. Bertelsen, G. M. Handel, B. G. Spars and P. H. Wallman. Chevron Research Company, Richmond, CA. The Chevron STB Oil Shale Retort. Preprint No. 23-81. 46th Midyear Refining Meeting, Session on Synthetic Fuels Processing - Part I, May 13, 1981, Chicago, Illinois. American Petroleum Institute, Washington, DC 20037.

Tarman, P. B., H. L. Feldkircher, and S. A. Weil. Hydroretorting Process for Eastern Shale. Presented at the Society of Petroleum Engineers, Eastern Regional Meeting, October 1977, Paper No. SPE 6628, IGT, Chicago, Illinois, 1977.

Tisot, P. R. Physical Structure of Green River Oil Shale. USBM Report of Investigations 6184, 1963.

Tisot, P. R., and H. W. Sohns. Structural Deformation of Green River Oil Shale as it Relates to *In Situ* Retorting. USBM Report of Investigations 7576, 1971.

TOSCO Development Corporation, Denver, Colorado. Project Description Technical Report, Sand Wash Shale Oil Project. Uintah County, Utah. May 1982.

TRW. Denver Research Institute. An Engineering Analysis Report on the Union Retort B Process. Prepared for Industrial Environmental Research Laboratory, U.S.E.P.A., Cincinnati, Ohio 45268, under Contract No. 68-02-1881, March 1977.

TRW. Denver Research Institute. Management of Solid Waste Residuals from Oil shale Recovery Processes. Prepared for Industrial Environmental Research Laboratory, U.S.E.P.A., Cincinnati, Ohio 45268, under Contract No. 68-02-1881, May 1977.

TRW. Denver Research Institute. Trace Elements Associated with Oil Shale and its Processing. Prepared for Industrial Environmental Research Laboratory, U.S.E.P.A., Cincinnati, Ohio 45268, under Contract No. 68-02-1881, May 1977.

Union Oil Company of California, Energy Mining Division. Environmental Monitoring Plan Outline. Parachute Creek Shale Oil Program, Phase II, January 23, 1984. U.S. Patent 4037657.

Vanderborgh, N. E. Characterization of Oil Shales by Laser Induced Pyrolysis. FACSS, Atlantic City, N.J., Nov. 19, 1984.

Wildung, R. E., and J. M. Zachara. Geochemistry of Oil Shale Solid Waste Disposal. Proceedings of International Symposium, August 11-14, 1980. K. K. Peterson, Editor. Sponsored by the Oil Shale Task Force and U.S. Department of Energy. Colorado School of Mines Press, Golden, Colorado, 1981.

APPENDIX A

AUTO-OXIDATION POTENTIAL OF RAW AND SPENT SHALE AND THE SUGGESTED DESIGN OF PILES TO AVOID THE AUTO-IGNITION OF SHALES

A.1. Auto-oxidation Potential of raw and Spent Shales

At the present time, considerable effort is being devoted to commercialization of processes to produce liquid fuels from oil shale deposits in the western United States. The retorting of oil shale produces large quantities of solid waste. This material, mineral matter from which kerogen has been thermally removed to a varying extent, is referred to as retorted or spent oil shale. This spent oil shale contains a considerable amount of carbonaceous material. The amount of spent shale to be disposed of after retorting the raw shale is dependent upon the retorting technology, and retort efficiency. For example, a 50,000 tons per day retort, using 25 gallons per ton raw shale has been estimated to produce 42,500 tons per day of spent shale for disposal [Brown et al., September 1977]. Retorted shales from internal combustion gas retorts have carbon compositions of 2% to 3% and are soft and friable. Retorted shales from indirect heated retorts (Paraho indirect mode, TOSCO II, Union B) have a higher carbon content which may be reduced to less than 1% if the retorted shale is subsequently combusted.

Most developers are currently planning on disposing of the the spent shale, overburden and rejected raw shale fines in nearby canyons. Disposing of this material in landfills several hundred feet thick and covering several square miles each is a likely prospect. The phenomena of auto-oxidation, self-heating, and spontaneous combustion have long been observed in large masses of carbonaceous materials such as coal storage piles, coal mining refuse piles, and dump sites. Where spontaneous combustion has occurred, extinguishing measures have been difficult or impossible. Hence the potential of spontaneous combustion in spent oil shale disposal areas is a matter of serious environmental concern.

Most of the work in the area of auto-oxidation potential has been done on coals. Several factors have been found to have a significant effect on the rate of spontaneous heating of coal [Kim, 1977] as described below:

Air Flow Rate

The air flow rate is a complex factor because air both provides oxygen for oxidation of the coal and dissipates the heat generated by oxidation. A very high flow rate provides almost unlimited oxygen, but dissipates heat efficiently. A low flow rate restricts the amount of oxygen available, but allows heat generated to remain in the coal. A critical flow rate would be one that provides sufficient oxygen for widespread oxidation but does not dissipate the heat generated.

Particle size

Particle size has an inverse relationship to spontaneous heating. The smaller the particle size, the greater is the exposed surface area and the greater is the tendency toward spontaneous heating.

Rank

It is generally agreed that spontaneous combustion is a rank-related phenomenon. As the rank of coal decreases, the hazard of spontaneous heating increases. Lignites and subbituminous coals are most susceptible to spontaneous heating.

Changes in Moisture Content

The moisture content of the coal, or more exactly, changes in moisture content, affect the tendency of coal to spontaneous heating. Drying, lost of moisture, is an endothermic process and lowers the temperature of the coal; it also exposes more oxidative sites. Wetting, gain of moisture, is an exothermic process, and the heat liberated may be sufficient in itself to cause spontaneouts heating. For a given coal at temperatures below 212°F, the heat of wetting is greater than the heat of oxidation.

Temperature

The rate of coal oxidation is a direct function of temperature; the higher the temperature, the faster the rate at which coal reacts with oxygen. This is particularly important in areas where heat generated by oxidation accumulates, further accelerating the rate of oxidation.

Pyrite Content

The presence of the sulfur minerals pyrite and marcasite may accelerate spontaneous heating. Under certain conditions, the pyrite may swell and cause the coal to disintegrate, exposing more oxidative sites. If the pyrite is finely divided and can be rapidly converted to ferrous sulfate, the coal is more susceptible to spontaneous heating. Generally, the pyrite concentration must exceed 2 pct. before it has a significant effect.

The various methods used to study spontaneous heating are described in detail in the literature (Guney and Hodges, 1969], most are variations of the four basic methods described in the following paragraphs [Kim, 1977].

Adiabatic Calorimetry

The coal sample is placed in an insulated container or bath, and the whole system is heated to a preselected temperature. When air or oxygen is added, the temperature of the coal rises; the material surrounding the coal is heated so that its temperature coincides with the measured temperature of the coal. Since there is no heat loss to the surroundings, changes in coal temperature are measured accurately. The change in the temperature of the coal in a given time, the time needed to reach a preselected temperature, or the amount of heat generated per unit of time is used to evaluate the spontaneous heating potential of the coal.

Isothermal Calorimetry

In this method, a coal sample is placed in a large bath held at a constant temperature. Heat generated in the coal sample, by oxidation or wetting, is measured by thermocouples and dissipated in the relatively large heat sink. The measured rate of heat generation is correlated with the combustibility of the coal.

Oxygen Sorption

In the oxygen-sorption method, a coal sample is placed in a container and air or oxygen is added. In a closed system, gaseous reaction products are periodically removed, and the amount of air or O_2 that must be added to maintain the system at constant pressure is used to estimate the amount of oxygen absorbed. In a flow system, the flow rate and analysis of the effluent gas are used to estimate the amount of oxygen adsorbed by the coal. The temperature increase per unit of oxygen consumed indicates the coal's potential for spontaneous heating.

Temperature Differential

The coal sample is placed in a bath and heated at a constant rate; the temperature difference between the coal and the bath is measured. Initially, the temperature of the coal lags behind the bath temperature. When the coal begins to self-heat, the temperature of the coal will coincide with, then exceed, the temperature of the bath. Usually, some variant of a temperature differential-time relationship indicates the combustibility of the coal.

Most experimental studies use one of the four basic methods described, but other factors vary for each experiment. The coal samples vary, particularly in origin, amount, preparation, and particle size. The atmostphere is usually air or O_2 although N_2

or other inert gas may be used for baseline evaluation or to bring the coal to the starting temperature. The oxidizing medium used may be moist or dry, flowing or static. The initial temperature, final temperature, and heating rate also vary. In some case, the effluent gas is analyzed for CO, CO_2, O_2, CH_4, and other hydrocarbons to provide a more of its relatively simple adaption to the detection of spontaneous heating.

A readily determined, universally applicable index of combustibility would be the preferred method of evaluating liability to spontaneous heating. Although several indices of combustibility are proposed in the literature for coals, none is in general use. The most common indices are described in the following paragraphs [Kim, 1977].

Heating Rate

The temperature increase under controlled conditions, measured in degrees Centigrade per hour per gram (°C/hr/g). Another variant involves the measurement of the quantity of heat released, measured in calories per hour per gram (cal/hr/g). The greater the heating rate, the greater is the tendency to spontaneous heating. Two variations of this method are:

> Relative Heating Rate The heating rate relative to the heating rate of some standard sample.
>
> Dynamic Heating Rate Rate at which the temperature of the coal increases with respect to its surroundings within a given temperature range.

Crossing-Point Temperature

The temperature at which the temperature of the coal and a heated bath coincide, also called relative ignition temperature.

Ignition Temperature

The temperature at which the coal ignites. The ignition temperature at which the coal ignites. The ignition temperature is determined by observation; that is, the temperature at which an observer sees the coal fire. It cannot be exactly defined and, therefore, can only be used to determine relative spontaneity of the coals tested.

$CO/\Delta O_2$

The ratio of CO formation to oxygen adsorption, also called the "CO index." The increase in the concentration of CO and the decrease in the concentration of oxygen are related to the temperature of the coal. Monitoring air for CO and oxygen is the basis for a method of detecting spontaneous heating.

Combinations of the preceding indices also are used in an attempt to achieve greater accuracy. All of the indices are determined by a laboratory procedure and require standard conditions to obtain reproducible results. In some studies, the index of interest is compared to some internal standard; oxygen content of the coal, for instance, without mathematical correlation. In other studies, a simple ranking system is used to evaluate the coal's combustibility. Indices determined in the laboratory have not been compared to the actual incidence of spontaneous heating. Owing to the lack of an objective criterion and the diversity of experimental conditions under which the indices were developed, comparing various indices would be inaccurate and possibly misleading. No particular index has been shown to be significantly more accurate, and none is in general use. At present, the CO index is probably receiving the most interest in the United States. This is not because of demonstrated superiority as an index of combustibility, but because of its relatively simple adaptation to the detection of spontaneous heating. In many instances, evaluation of the hazards from spontaneous heating is based on previous experience with a given coal.

Recently Green of Research Triangle Institute (RTI) conducted experimental work on measuring auto-oxidation potential of raw and retorted oil shale for the U.S. EPA [EPA-600/2-84-153, 1984]. This study was conducted to assess the potential spontaneous combustion hazard of solid waste streams produced in the processing of oil shale. In additon, the utility and precision of various test methods to assess this hazard were assessed. This work is the most comprehensive work done to measure the autoignition potential of raw and spent shales and is summarized below:

A.1.1. RTI Study On Auto-oxidation Potential of Raw and Retorted Oil Shale

Factors which influence the tendency of a storage pile to self-heat and eventually ignite can be grouped into two main categories. The first category includes those properties which are peculiar to the solid itself: reactivity toward oxygen, and heat release as a function of temperature. The second group of factors are those relating to the pile and its construction: overall dimensions, particle size, degree of compaction, homogeneity, ambient temperature, temperature of placed materials, precipitation, wind speed, etc. It is quickly seen that pile characteristics are going to be more difficult to measure and most likely subject to more variation than the properties of the solid itself.

In this study, an investigation of laboratory methods of determining spontaneous combustion tendencies was conducted. These methods were then applied to raw and retorted oil shale samples to determine the relative hazards presented by these materials.

In addition, several coal samples were tested by the same methods so that the hazards of the oil shale materials could be related to the better known phenomenon of self heating in coal storage piles.

Retorted shale samples from the Lurgi, TOSCO II, Paraho direct-mode, Hytort and Union B processes were tested. A raw shale from Federal lease tract C-a in Colorado, two raw shale samples from Federal lease tract Ua/Ub in Utah, Wyoming subbituminous coal, Western Kentucky #9 bituminous coal and Pocahontas #3 (Virginia) bituminous coal were also tested. Sulfur and organic carbon contents and heating values of these materials are given in Table A-1. Heat capacities of these materials, as determined by differential scanning calorimetry are given in Table A-2.

RTI tested shale samples for auto-oxidation potential by various methods such as: nonadiabatic oxygen absorption test, adiabatic oxygen absorption test, differential scanning calorimetry test, isothermal pressure differential scanning calorimetry test, peroxide test and thermal graviometric analysis testing. The best method found involved a differential scanning calorimeter test and a nonadiabatic oxygen absorption test. In the former case, endothermic activity was monitored; in the latter, changes in gas composition (outlet vs inlet) were monitored.

A.1.1.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) involves the measurement of the heat evolved or absorbed by a sample at a given temperature relative to a known reference material at the same temperature. When the temperature is increased or decreased, heat effects arise from differences in specific heats, phase changes and chemical reactions. Low temperature oxidation is an exothermic reaction. When spontaneous heating occurs, the heat produced by this reaction (and other exothermic reactions including the heat of wetting) is greater than the heat which is rejected to the surroundings and the material which is oxidizing increase in temperature. As the temperature of the material increases, the rate of oxidation increases and, in some cases, a rapid temperature increase then occurs.

DSC data, obtained while the temperature of the sample and reference are increased at a slow constant rate, indicate the difference in heat flow between sample and reference as a function of temperature. When the reference is an empty sample pan of equal mass and specific heat to the pan in which the sample is held, the net heat effect is that produced by the sample. When the temperature of the apparatus is restricted to eliminate the possibility of phase changes in the sample, endothermic effects are associated with the heat capacity of the sample, and with some materials, such effects as drying, desorption of gases, and devolatilization. Exothermic effects in excess of the sample heat capacity are associated with exothermic chemical reactions.

TABLE A-1. DESCRIPTION OF SAMPLES TESTED BY RTI

Materal (-325 mesh)	Total sulfur wt. % dry basis	Organic carbon % dry basis	Higher heating value Btu/lb dry basis
Western Kentucky #9 Bituminous Coal	3.73	61	13,050
Pocahontas #3 Bituminous Coal	0.65	69	12,120
Wyoming Subbituminous Coal	0.63	64	11,560
Utah Raw Shale (66 GPT)	1.85	28	6,240
Utah Raw Shale (28 GPT)	0.75	11	2,090
C-a Raw Shale	0.98	5.2	878
TOSCO II Retorted Shale	0.58	3.5	433
Hytort Retorted Shale	2.40	3.8	420
Paraho Retorted Shale	0.57	3.1	188
Union Shale Mixture	0.68	4.1	209
Lurgi Retorted Shale	0.86	0.13	44

Source: EPA-600/2-84-153, 1984

TABLE A-2. MEAN HEAT CAPACITY OF COAL AND SHALE MATERIALS BASED ON INITIAL SAMPLE WEIGHT (J/G, -325 MESH)

Materal	Temperature range, °C		
	25 - 200	25 - 400	25 - 600
C-a Raw Shale	0.76	0.72	0.73
Utah Raw Shale (66 GPT)	2.18	2.13	2.56
Utah Raw Shale (28 GPT)	1.17	1.15	1.23
Hytort Retorted Shale	1.08	1.03	1.17
Pocahontas #3 Bituminous Coal	1.19	1.28	1.40
Western Kentuck #9 Bituminous Coal	0.69	0.47	0.44
Wyoming Subbituminous Coal	1.28	0.67	0.63
Lurgi Retorted Shale	0.82	0.87	0.92
TOSCO II Retorted Shale	0.39	0.89	0.86
Paraho Retorted Shale	0.73	0.71	0.66
Union Shale Mixture	2.57	1.75	1.60

Source: EPA-600/2-84-153, 1984

Samples were tested in a DuPont Instruments Model 951 differential scanning calorimeter equipped with a standard low pressure cell. The calorimeter was coupled to a DuPont Instruments Model 1090/1092 thermal analyzer which permitted temperature programming and data acquisition/playback using magnetic disk storage. Samples of between 17 and 54 mg were used. Variations in sample mass for the different materials tested were primrily due to differences in bulk density. Samples were loaded into open aluminum pans; the pans were completely filled to the top edge and excess material was removed so that the sample surface was level. An empty pan of comparable mass (and heat capacity) was used as a reference in all tests.

With air flowing through the cell, a preweighed sample in a tared aluminum pan was placed on the sample thermocouple disk and an empty sample pan was placed on the reference thermocouple disk.

The test was conducted by programming the heater to increase the temperature of the Constantan disk to which sample and reference thermocouples were attached. A precisely controlled heating ramp of 2°C per minute was followed from slightly above ambient temperatures (25°-30°C). Different samples were heated to different final temperatures (380°-550°C) but in all cases the test was continued to the end of the exotherm. Exothermic reactions were sensed by a slight lead in temperature of the sample thermocouple over the reference thermocouple. The instrument was calibrated to convert this lead into an actual heat effect.

The most important measurement relating DSC data to spontaneous heating behavior is the onset temperature of the exothermic oxidation reaction. When an exotherm is observed while a sample is being heated, this temperature is characterized by extrapolating the slope of the leading edge of the exothermic peak to the baseline. It is assumed that the lower this temperature is, the greater the tendency of the material to spontaneously heat. This provided a means for empirically ranking materials of unknown self-heating potential by comparison to materials of known heating potential. The results of this test are summarized in Tables A-3 and A-4. The Wyoming subbituminous and Western Kentucky bituminous coals exhibited the earliest exothermic onset temperatures followed by the 66 gallon/ton raw Utah shale. The low volatility bituminous Pocahontas #3 coal was less reactive than any of the raw western shales which were tested. The carbonaceous retorted shale samples exhibited considerably higher exothermic onset temperatures than the raw shale indicating that they present less of a spontaneous heating hazard than the raw shale and much less than the coal. Decarbonized shale from the Lurgi process was also tested but absolutely no exothermic reaction was observed at temperatures up to 550°C. The Hytort retorted shale was extremely unreactive, exhibiting an exothermic onset temperature higher than that of any of the retorted shale samples except for the Lurgi retorted shale.

TABLE A-3. EXOTHERMIC ONSET TEMPERATURE OBSERVED IN OXIDATION OF COAL, OIL SHALE AND RETORTED OIL SHALE (2°c/minute heating ramp, -325 mesh)

Materal	Atmosphere	Temperature °C
Wyoming Subbituminous Coal	Humid air	190
Wyoming Subbituminous Coal	Dry air	190
Western Kentucky #9 Bituminous Coal	Humid air	190
Western Kentucky #9 Bituminous Coal	Dry air	193
Utah Raw Shale (66 GPT)	Dry air	211
C-a Raw Shale	Humid air	225
C-a Raw Shale	Dry air	226
Utah Raw Shale (28 GPT)	Dry air	227
Pocahontas #3 Bituminous Coal	Dry air	230
TOSCO Retorted Shale	Humid air	296
Paraho Retorted Shale	Dry air	300
Paraho Retorted Shale	Humid air	300
Paraho Retorted Shale (-48 + 100 mesh)	Humid air	300
Paraho Retorted Shale (-48 + 100 mesh)	Dry air	302
TOSCO II Retorted Shale	Dry air	306
Union Shale Mixture	Dry air	331
Hytort Retorted Shale	Dry air	357
Lurgi Retorted Shale	Dry air	-[a]
Lurgi Retorted Shale	Humid air	-[a]

[a] No exoterm observed up to 550°C.

Source: EPA-600/2-84-153, 1984

TABLE A-4. MAGNITUDE OF EXOTHERMIC REACTION OF COAL, OIL SHALE AND RETORTED OIL SHALE (2°C/minute heating ramp, -325 mesh)

Materal	Atmosphere	Exotherm J/g	Temperature range, °C
Bituminous Coal (Pocahontas #3)	Dry air	15,700	150-575
Bituminous Coal (W. Kentucky #9)	Dry air	13,800	90-550
Bituminous Coal (W. Kentucky #9)	Humid air	13,800	120-550
Sub-Bituminous Coal (Wyoming)	Humid air	11,200	50-440
Sub-Bituminous Coal (Wyoming)	Dry air	10,900	50-550
Utah (66 GPT) Raw Shale	Dry air	8,320	125-420
Utah (28 GPT) Raw Shale	Dry air	2,990	125-575
Hytort Retorted Shale	Dry air	1,340	175-575
Raw Shale (C-a)	Humid air	1,050	125-550
Raw Shale (C-a)	Dry air	920	160-480
TOSCO II Retorted Shale	Humid air	880	125-550
Union Shale Mixture	Dry air	860	200-575
TOSCO II Retorted Shale	Dry air	560	160-410
Paraho Retorted Shale	Humid air	490	175-410
Paraho Retorted Shale	Dry air	480	150-550
Paraho Retorted Shale (-48 +100 mesh)	Humid air	470	175-550
Paraho Retorted Shale (-48 +100 mesh)	Dry air	430	175-550
Lurgi Retorted Shale	Dry air	0	30-550
Lurgi Retorted Shale	Humid air	0	30-550

Source: EPA-600/2-84-153, 1984

A.1.1.2 Nonadiabatic Oxygen Absorption Test

The materials described above were also subjected to a nonadiabatic oxygen absorption test [Schmeling et al., 1978]. In this test 100 g samples of material were placed in a glass cell. Humidified air at 60 cc/min was passed through the cell and the temperature of the cell and contents were increased at a rate of 25°C/hour. The exhaust gas from the cell was analyzed chromatographically; the depletion of oxygen and increased levels of carbon dioxide were used as an indicator of reactivity.

Based on the gas analysis, a spontaneous combustion liability index (the S index) was calculated. The formula for this index was devised by Schmeling and is based on the conversion of oxygen in the inlet gas to CO_2.

$$S = \frac{h_1 + h_2}{2}(x_1) \quad \frac{h_2 + h_3}{2}(x_1)$$

where S = the spontaneous combustion index.
h_1 = 21 - oxygen concentration at 125°C.
h_2 = 21 - oxygen concentration at 150°C.
h_3 = 21 - oxygen concentration at 175°C.
x_1 = carbon dioxide concentration at 150°C - carbon dioxide concentration at 125°C.
x_2 = carbon dioxide concentration at 175°C - carbon dioxide concentration at 150°C.

All concentrations are expressed in volume percent.

The results of this test are summarized in Table A-5. The test indicated that the Wyoming subbituminous coal was by far the most reactive material with an S index of 108 in the -48+100 particle size test and an S index of 165 when tested in the -325 particle size. This is consistent with the generally observed phenomena of spontaneous heating in low rank coals. The criterion, adopted by Schmeling; that materials with S indices greater than 30 (for the -48+100 mesh size) are dangerous, also puts the Western Kentucky No. 9 bituminous coal (S = 37.5) in this category. As would be expected from historical observations of spontaneous combustion, the bituminous coals are much less dangerous than the subbituminous coal.

The tests indicated, as expected, that the retorted shales are less likely to spontaneously combust than any of the coals or raw shales. The three coals rank in the order expected from past experience and larger scale testing. The raw shales exhibit oxygen absorption behavior which ranks with their energy content. (The richer Utah shale has a higher S index than the leaner Utah shale and the three western shales follow the same order in S index as in higher heating value).

TABLE A-5. SPONTANEOUS COMBUSTION INDEX AND CALCULATION PARAMETERS OF MATERIALS SUBJECTED TO NONADIABATIC TEST (TESTED DRY)

Material (-325 mesh unless stated)	S	h_1	h_2	h_3	X_1	X_2
Wyoming Subbituminous Coal	165	9.44	17.42	20.97	4.48	5.48
Wyoming Subbituminous Coal (-48 + 100 mesh)	108	3.55	17.60	20.88	2.80	4.10
Raw Utah Shale (66 GPT)	86	7.41	19.7	20.8	3.56	1.86
W. Kentucky #9 Bituminous Coal	60	2.97	12.59	20.87	1.16	3.05
Raw Utah Shale (28 GPT)	44	1.55	8.49	18.2	1.10	2.88
Pocahontas #3 Bituminous Coal	42	3.43	11.2	21.0	1.03	2.13
W. Kentucky #9 Bituminous Coal (-48 + 100 mesh)	37.5	4.85	12.34	20.35	1.13	1.70
Raw Shale, C-a (-48 + 100 mesh)	6.89	0.45	2.60	6.55	0.23	1.43
Raw Shale, C-a	5.59	1.12	2.50	6.09	0.17	1.23
Union Shale Mixture	4.6	0.41	3.00	6.37	0.61	0.76
Hytort Retorted Shale	3.8	0.90	3.14	5.26	0.43	0.68
TOSCO II Retorted Shale (-48 + 100 mesh)	3.60	1.10	1.44	2.79	0.22	1.57
TOSCO II Retorted Shale	1.38	0.57	1.28	2.02	0.08	0.79
Paraho Retorted Shale	0.27	0.10	0.47	0.78	0.01	0.42
Paraho Retorted Shale (-48 + 100 mesh)	0.21	0.68	0.84	1.04	0.02	0.21
Lurgi Retorted Shale	0.00	0.38	-0.04	0.00	0.00	0.00
Lurgi Retorted Shale (-200 + 325 mesh)	0.00	0.32	0.14	0.15	0.00	0.01

Source: EPA-600/2-84-153, 1984

KEY

S = the spontaneous combustion index.

h_1 = 21 - oxygen concentration at 125°C.

h_2 = 21 - oxygen concentration at 150°C.

h_3 = 21 - oxygen concentration at 175°C.

X_1 = carbon dioxide concentration 150°C - carbon dioxide concentration at 125°C.

X_2 = carbon dioxide concentration at 175°C - carbon dioxide concentration at 150°C.

While none of the raw shales rank as high as the subbituminous coal, the richer (66 GPT) Utah shale ranks intermediate between it and the high volatility Western Kentucky #9 bituminous coal and the leaner (28 GPT) Utah Shale ranks intermediate between the Western Kentucky #9 coal and the low volatility Pocahontas #3 bituminous coal. On the basis of this test, the raw sales present a hazard of spontaneous combustion on the order of bituminous coals, and the greater the energy content of the shale, the greater is the tendency for spontaneous combustion. All of the retorted shales tested rank well below the bituminous coals in spontaneous combustion risk based on Schmeling's index.

A.1.1.3 Conclusions From RTI Study

It must be noted that the results reported are based on a very limited number of samples of raw and retorted shale. Substantial variations in composition of raw shales occur with geographic and stratagraphic location. The retorted shale samples came from pilot plant operations which may not be completely representitive of commercial operation. Hence it is strongly recommended that actual samples of waste materials proposed for field disposal be tested to determine their actual spontaneous combustion hazard.

Retorted shales investigated in the study are unlikely to present a spontaneous combustion hazard if properly handled. These include retorted shales from the Paraho direct, TOSCO II, Hytort, and Lurgi processes and a mixture of retorted shale, raw shale "fines," and sulfur from the Union B process. These materials proved to be far less reactive than Pocahontas #3 low-volatility bituminous coal which is generally regarded at the low end of the spectrum of coals susceptible to spontaneous heating. This conclusion was based on the basis of both the exothermic onset temperature, as determined by differential scanning calorimetry, and the nonadiabatic oxygen absorption test, and supported by TGA weight loss data. The Lurgi retorted shale is non-combustible and could not burn even if an attempt was made to ignite it.

The raw western shales, while not as liable to ignite as the Wyoming Smith-Roland subbituminous coal (which is generally placed at the higher end of the spectrum of coals susceptible to spontaneous heating) present a potential hazard. The richer of the Utah shale samples (66 GPT) is particularly reactive, falling between the Wyoming subbituminous and the Western Kentucky high volatility bituminous coal (of intermedial reactivity with regard to coal) in the nonadiabatic oxygen absorption test. In the DSC test, it falls below the Western Kentucky coal but above the relatively unreactive Pocahontas #3 coal. In the TGA weight loss test (based on mass remaining after heating to 300°C) a greater weight loss is observed with this sample than with the Western Kentucky bituminous coal.

The leaner Utah shale (28 GPT) is intermediate in tendency to autoignite between the Western Kentucky coal and the Pocahontas #3 coal in both the nonadiabatic oxygen absorption test and the DSC test (ranked by exothermic onset temperature). This material falls below the coal samples in the TGA weight loss tests. By Schmeling's criteria (S index > 30), this is also a potential hazard. The C-a shale has about the same exothermic onset temperature as the leaner Utah shale (i.e., intermediate between the Western Kentucky and Pocahontas bituminous coals, but ranks considerably lower than the Pocahontas coal in the nonadiabatic oxygen absorption test with an S index of about 6). This is probably the least reactive of the three western raw shales tested but should still be regarded as posing potential problems.

The results of the study suggest that carbonaceous retorted oil shale poses less hazard of spontaneous combustion than bituminous coal and it is logical that the more severe the retorting process and the more complete the removal of the organic matter, the less reactive the resulting waste product will be. This does not imply that the risk of spontaneous combustion can be ignored but rather that the risk should be low if proper disposal practices are followed. Good practice would likely include cooling before disposal, compaction in lifts, and excluding air flow into the pile.

Decarbonized shales, such as the Lurgi decarbonized retroted shale, are essentially inert since substantially all of the energy content has been removed. Such shales should present no hazard of spontaneous combustion.

On the basis of DSC testing, codisposal of byproduct elemental sulfur with retorted oil shale will not increase the hazard of spontaneous combustion of the mixture. The mixing of raw shale fines with retorted oil shale for disposal should be approached very cautiously and preferably be avoided. The addition of as little as 5 percent raw shale fines, appears to lower the exothermic onset temperature of the mixture to approximately that of the fines themselves. Although the energy available in the mixture is much less than that of the raw shale fines, the potential for spontaneous combustion may be significantly increased as compared to the retorted shale alone and may in fact be as great as that of the raw shale fines alone. For example the addition of as little as 5 percent raw shale fines (Utah 28 GPT) lowered the exothermic onset temperature of Paraho retorted shale to that of the raw shale fines alone. However it must be emphasized that the data on this point are somewhat conflicting. The Union B shale mixture which contained 5.47 weight percent raw shale fines behaved in a manner similar to other carbonaceous retorted oil shales which did not include a mixture of raw shale fines. Hence it is recommened that anyone proposing disposal of retorted and raw shale mixtures should evaluate their particular mixture to define its properties. It is considered likely that for each specific retorted raw shale mixture there is a unique value of raw to retorted shale ratio which if exceeded will cause the mixture to assume the properties of the raw shale.

The raw western shales present a potential hazard, but if stored and disposed of under conditions suitable for long term storage of reactive coals, then they should pose no greater risk than such coals. Ideally, however, raw shales should be processed for energy recovery to the greatest extent possible. Material produced during crushing operations that is too small for retorting would be preferably subject to combustion for production of process heat, or if feasible, agglomerated with a binder to a size where it could be retorted for maximum energy recovery.

Of the test methods used in the RTI study, the differential scanning calorimetry test and the nonadiabatic oxygen absorption test appear to be the most meaningful. These tests were reproducible and, when the tests were applied to coal samples, the results conformed to generally observed rankings of spontaneous combustion potential. Of the other tests considered, the peroxide test was technically unsound; pressure differential scanning calorimetry and adiabatic oxygen absorption tests did not produce useful, reproducible results in the course of this particular study. These methods may, however, after further development be made useful. The thermogravimetric analysis weight loss test, while potentially useful in characterizing samples was found unsuitable as results for coal samples did not conform to generally accepted spontaneous combustion rankings and the retorted shale samples produced an insufficient reponse to evaluate.

A summary of results obtained in the differential scanning calorimetry and nonadiabatic oxygen absorption testing is given in Table A-6. As no reference standards are available for the test parameters which were determined, the accuracy of these tests cannot be determined. However, the ranking of the materials can be used as an indicator of relative spontaneous combustion hazard.

In summary, the carbonaceous retorted oil shale samples appear to present less hazard of spontaneous combustion than bituminous coal. None of the raw shales were found to present as great a hazard as Wyoming subbituminous coal. However, the two raw Utah shale samples tested were found to present hazards exceeding those of less reactive bituminous coals. These materials represent a potential hazard, but if stored and disposed of under conditions suitable for long-term storage of reactive coals, should not spontaneously combust. The co-disposal of raw and retorted shale should be approached cautiously and preferably be avoided if possible as the presence of raw shale increases the energy contents of the mixture and in some cases decreased the temperature at which exothermic activity was observed. Co-disposal of byproduct sulfur with retorted shale appears to cause no increase in risk of spontaneous combustion (but may lead to leaching problems).

TABLE A-6. SUMMARY OF RESULTS FROM DIFFERENTIAL SCANNING CALORIMETRY AND NONADIABATIC OXYGEN ABSORPTION TESTING

Materal	DSC[a] Onset, °C	DSC[a] Exotherm, J/g	Nonadiabatic test S index
Wyoming Subbituminous Coal	190	10,900	165
Western Kentucky #9 Bituminous Coal	193	13,800	60
Utah Raw Shale (66 GPT)	211	8,320	86
C-a Raw Shale	226	920	5.6
Utah Raw Shale (28 GPT)	227	2,990	44
Pocahontas #3 Bituminous Coal	230	15,700	42
Paraho Retorted Shale	300	480	0.27
TOSCO II Retorted Shale	306	560	1.4
Union Shale Mixture	321	860	4.6
Hytort Retorted Shale	357	1,340	3.8
Lurgi Retorted Shale	-[b]	~0	0.00

[a] Tested in dry air, particle size: -325 mesh.

[b] No extherm observed to 550°C.

Source: EPA-600/2-84-153, 1984

A.2 Raw and Spent Shale Storage Design To Avoid Auto-Ignition

As described earlier, the carbonaceous retorted oil shale samples appear to present less hazard of spontaneous combustion than bituminous coal. None of the raw shales were found to present as great a hazard as Wyoming subbituminous coal. These materials represent a potential hazard, but if stored, and disposed of under conditions suitable for long-term storage of reactive coals, should not spontaneously combust. The co-disposal of raw and retorted shale should be approached cautiously and preferably be avoided if possible.

There has been no work in the area of practices of storage of raw and spent shales. The work has been done in the area of coal storage practices based on experience from the coal storage piles auto-ignition behavior. As raw and spent shale present less hazard of auto-ignition than coal, the use of coal storage designs should prevent auto-ignition phenomena in raw and spent shales.

A.2.1 Coal Storage Pile Design to Avoid Auto-ignition Phenomena

Since spontaneous combustion is a serious hazard in stockpiling low-rank coals, it would be well to outline the mechanism of such combustion. Given a low-rank coal and a high-rank coal, the greater moisture content and reactivity of the lower-rank coal make it the more susceptible to spontaneous combustion and therefore more difficult to stockpile safely. Low-rank coals have a greater tendency than high rank coals to slack and absorb oxygen. Although loss of moisture is ultimately beneficial in that it actually results in an increase in heating value, the absorption of oxygen is detrimental. The slight weight increase represents a loss in B.t.u. per pound, and the reaction is accompanied by a heat release, which can cause an increased rate of oxygen absorption. This oxygen absorption is further aggravated by the smaller particle size and associated large increase in total surface area resulting from the slacking. Unless checked, the exothermic reaction may eventually result in actual combustion.

In a surface storage pile the rate of oxygen absorption can be retarded only be restricting the movement of air into and out of the pile. These air movements are caused by:

1. Convection currents within the pile - the "chimney effect" of drawing fresh air in at the sides and expelling pile gases at the top.
2. Barometric pressure changes.
3. Changes in ambient air temperature.
4. Differential wind pressures on various portions of the pile surface.

Convection currents may always be considered to exist in any pile. Their rate of movement, however, will vary greatly depending on the degree of compaction of the coal and the presence or absence of air channels within the coal mass. Convection currents may be minimized by avoiding segregation and by thorough compaction, which is most effective when applied to thin increments as the pile is formed. The effects of compaction are shown in Table A-7 [Allen and Parry, 1954].

TABLE A-7. EFFECT OF COMPACTION IN REDUCING THE VOLUME OF AIR ENTERING OR LEAVING A COAL MASS IN RESPONSE TO BAROMETRIC PRESSURE CHANGE[a]

Bulk density, lb/ft^3	Total volume, coal and air, cu ft	Volume of coal, cu ft	Volume of air, cu ft	Volume of air entering coal mass, cu ft	Heat released by complete combustion of coal with entering air, Btu
40	5,000,000	2,500,000	2,500,000	125,000	12,500,000
45	4,445,000	2,500,000	1,945,000	96,700	9,670,000
50	4,400,000	2,500,000	1,500,000	74,800	7,480,000
55	3,636,000	2,500,000	1,136,000	55,660	5,566,000
60	3,333,000	2,500,000	833,000	41,650	4,165,000
65	3,078,000	2,500,000	578,000	28,900	2,890,000
70	2,860,000	2,500,000	360,000	18,000	1,800,000
75	2,666,000	2,500,000	166,000	8,280	828,000
80	2,500,000	2,500,000	0	0	0

[a] Assuming 100,000 tons of coal in storage and 5 percent increase in barometric pressure.

Source: Allen and Parry, 1954

Although barametric pressure changes cannot be controlled, the resultant movement of air into and out of the pile can be minimized by thoroughly compacting the coal mass, thus reducing the volume of air within the pile.

Ambient air temperature changes cannot be controlled but the resultant air movement into and out of the pile, although slight, can be minimized by reducing the air volume of the pile.

Air currents set up in the pile by differential wind pressures are best suppressed by avoiding segregation, adequate compaction, and smoothing the pile surface.

When the movement of air into and out of a pile is restricted as outlined above, the absorption of oxygen from the air within the pile renders the pile gases inert thus effectively checking the dangerous cycle of oxygen absorption, heat release and increased rate of oxygen absorption.

In reviewing the various methods of restricting air movements within the pile it is evident that compaction and avoidance of segregation are the most important factors in combating every cause of air circulation. Both must be accomplished to achieve trouble-free storage. Omission of either one or the other could result in eventual heating and combustion, since the success of the storage effort will be no better than the poorest piling technique employed.

Numerous methods of sealing storage piles of low-rank coals have been attempted [Allen and Parry 1954]. Since the most desirable seal is one which permits the gradual infiltration of air over the entire pile surface, asphalt seals are considered to be undesirable because they effectively seal most of the pile surface but leave some small openings, which act as orifices for relatively high velocity air movements into and out of the pile. Packed earth seals are subject to the same criticism, plus the problems of maintenance of of the seal and recovery of clean coal. Ash and cinder coverings are considered to be ineffective and merely contaminate the coal. The cheapest and most effective seal appears to be the well slacked coal on the surface of the pile. This seal, which represents no contamination problem, will absorb oxygen from the entering air so that air reaching the interior of the pile will be virtually inert.

There are some other considerations which can be taken into account when designing a coal pile storage [Lowry, 1954] and these are summarized below:

1. Storage area should be level, firm, well drained, and free of fences, piers, etc.

2. Build up the piles in increments not exceeding 1 to 2 ft. in depth.

3. Thoroughly compact each increment before placing additional coal on the pile. This compaction should be applied to the entire pile top, sides and edges.

4. Maintain the side slope at 14° or less to prevent segregation and to facilitate the compaction. Though one study [Davis and Boegly, January 1978] has recently suggested a side slope up to 30° or less.

5. Decreased height of storage piles results in decreased probability of spontaneous combustion since (a) the effective resistance to heat flow is lower which results in the faster heat of oxidation dissipation with less rise in temperature (b) lower piles tend to decrease the amount of segregation of sizes when coal is piled carelessly and (c) it is easier to remove "hot spots" when they occur.

6. Segregation of sizes should be avoided since many fires occur near the boundaries of zones of coarse coal that apparently act as chimneys for conducting air into the pile.

7. Preferably coal should not be piled in hot weather since many fires apparently are due to this cause.

8. A shipment of coal that is wet should not be piled with other coal.

9. Coals from different sources should not be stored in a common pile.

10. Care should be taken to keep out extranenous material which may cause fires.

11. After storage the temperature of a pile should be determined regularly by means of thermometers in previously installed pipes. The extremely local nature of "hot spots" makes it necessary to test at points on 10 to 20 feet centers. If temperatures of 140 to 150°F are found, the temperature of the coal near these points should be taken on 5 foot centers.

Although these techniques deal with the storage of low rank highly reactive coals, it is obvious that any stockpiling technique resulting in trouble-free storage of these fuels would be even safer for storing less reactive raw and spent shales.

APPENDIX B
USE OF SPENT OIL SHALE AS A LINER MATERIAL AT SPENT SHALE DISPOSAL SITES

Prepared by:

William J. Culbertson, Jr.
Charles H. Habenicht
Denver Research Institute
Chemical and Materials Sciences Division
University of Denver
Denver, Colorado 80208

For:

Monsanto Company
Dayton Laboratory
1515 Nicholas Road
Dayton, Ohio 45407

Contract No. EPA 68-01-6487

CONTENTS

Page

I. INTRODUCTION AND SCOPE 1
- A. Object 1
- B. Approach. 2
- C. Experimental Plan and Independent Variables Used. 3

II. DISCUSSION OF RESULTS 7
- A. Permeability 7
- B. Peak Angle of Internal Friction O_p Related to Self Healing and Its Trade Off With Permeability 17
- C. Residual Shear Strength and Critical Void Ratio Related to Slope Stability. 19
- D. Brittleness Index Related to Cementation and Permeability 19
- E. Relation of Peak Friction Angle O_p and Brittleness Index BI with Initial Torsional Stiffness and Shear Modulus G. 20
- F. Relation of Peak Friction Angle with Twist at Peak Strength 24
- G. Relation of Peak Friction Angle and Squashiness Index with Cured Void Ratio. 24
- H. Hydrate Species Determined by EGA. 28
- I. Secondary Compression Index C Related to Cementation and Mellowing 31
- J. Indirect Tensile Strength (Brazilian) Test . . . 33
- K. Compression Index. 36

III. CONCLUSIONS AND RECOMMENDATIONS 41

IV. REFERENCES. 43

LIST OF TABLES

Table B- Page

I 1 Experimental Design - TOSCO II. Lurgi, and Mixtures of Mellowed TOSCO and Mellowed Lurgi with Burned and Unburned TOSCO and Unmellowed Lurgi Spent Shale. 5

II 1. Pneumatic Arm Oedometer Results from Fresh Specimens: Void Ratios e and Compression Indices C_c 37

LIST OF FIGURES

Figures B- Page

II 1. Permeability of Mixtures of Burned TOSCO and Unburned TOSCO Spent Shale after Approximately Four Weeks Curing in Spring Oedometers 8

II 2. Permeability of 100% TOSCO II Spent Shale (TOSCO 100) . . . 9

II 3. Permeability of 90% TOSCO II - 10% Burned TOSCO Spent Shale (TOSCO 90). 9

II 4. Permeability of 80% TOSCO II - 20% Burned TOSCO Spent Shale (TOSCO 80). 9

II 5. Permeability of 70% TOSCO II - 30% Burned TOSCO Spent Shale (TOSCO 70). 10

II 6. Permeability of Lurgi Spent Shale 10

II 7. Permeability of Mellowed Lurgi (M14) mixed into Lurgi and Mellowed Burned TOSCO (M-15) Mixed into TOSCO II and into Burned TOSCO Spent Shale. 11

II 8. Mineral Grain Density vs Time for TOSCO 100 Spent Shale . . 12

II 9. Mineral Grain Density vs time for TOSCO 90 Spent Shale. . . 12

II 10. Mineral Grain Density vs Time for TOSCO 80 Spent Shale. . . 13

II 11. Mineral Grain Density vs Time for TOSCO 70 Spent Shale. . . 13

II 12. Mineral Grain Density vs time for Lurgi Spent Shale 14

II 13. Permeability of Spent Shales Correlated with Void Ratio . . 16

II 14. Permeability Of TOSCO Spent Shale Mixtures Correlated with Peak Friction Angle. 18

II 15. Permeability of Lurgi Spent Shale Correlated with Peak Friction Angle 18

II 16. Brittleness Index Correlated with Peak Friction Angle . . . 21

II 17. Permeability Compared with Brittleness Index. 22

II 18. Peak Friction Angle Compared with Initial Shear Modulus G 23

II 19. Brittleness Index Compared with Initial Shear Modulus G 25

II 20. Extent of Twist at Peak Strength Correlated with Peak Friction Angle. 20

II 21. Peak Friction Angle of TOSCO 100 vs Void Ratio. 27

II 22. Peak Friction Angle of TOSCO 90 vs Void Ratio 27

II 23. Peak Friction Angle of TOSCO 80 vs Void Ratio 27

II 24. Peak Friction Angle of TOSCO 70 vs Void Ratio 27

II 25. EGA Hydrate Water Peak of Tobermorite and Ettringite vs Time for TOSCO 100, 90, and 70 Specimens 29

II 26. Peak Friction Angle vs Time for TOSCO 100, 90, and 70 Specimens 29

II 27. Initial Torsional Stiffness vs 115 to 135°C EGA Peak Height 30

II 28. Twist at Peak Strength vs 115 to 135°C EGA Peak Height. . . 30

II 29. Final C at 45° Peak Friction Angle for Oedometer Specimens of Various Spent Shale Mixtures 32

II 30. Final C vs Peak Friction Angle for TOSCO 100 Specimens . . 32

II 31. Final C vs Peak Friction Angle for TOSCO 90 Specimens. . . 32

II 32. Final C vs Peak Friction Angle for TOSCO 80 Specimens. . . 32

II 33. Final C vs Peak Friction Angle for TOSCO 70 Specimens. . . 32

II 34. Final C vs Peak Friction Angle for Lurgi Specimens 32

II 35. Torsion Test Twist at Peak Strength vs Brazil Tensile Strength. 34

II 36. Brazil Tensile Strain At Failure vs Torsion Test Twist at Peak Strength. 34

II 37. Brazil Tensile Strength vs Initial Water Content. 35

II 38. Compression Index of Fresh Specimens for Loading Increment 155 to 310 PSI. 35

SYMBOLS AND ABBREVIATIONS

The following symbols have been used in this Appendix.

TA TOS100 TOSCO 100 100% TOSCO II	Fluidized bed burned TOSCO II spent shale from TOSCO Rocky Flats site (from drum number TA). Unburned scalped retorted spent shale from a pilot size TOSCO II retort at the TOSCO Rock Flats site.
TOS90 TOSCO 90	A mixture of 90% unburned TOSCO II spent shale with 10% of burned spent shale from a pilot size fluidized bed burner fed TOSCO II spent shale at the TOSCO Rocky Flats site.
TOS 80 TOSCO 80	A mixture of 80% unburned TOSCO II spent shale with 20% of the burned spent shale.
TOS 70 TOSCO 70	A mixture of 70% unburned TOSCO II spent shale with 30% of the burned spent shale.
MEL	Autoclave mellowed material.
△	Triangle data points on graphs are usually for standard proctor specimens.
□	Square data points on graphs are usually for modified proctor specimens.
51	Number by data point on graph signifies oedometer loading number of specimen tested.
24%	Percentage figure by data point on graph signifies percent water dry basis added to spent shale mix before loading oedometer.
PSI	Pounds per square inch
Gm	Grams mass
cc	Cubic centimeters
Lb	Pounds
EGA	Evolved gas analysis
e	Void ratio
C_α	Secondary compression index $= \frac{d\,e}{d \log t}$ = slope of void ratio vs logarathim of time plot of secondary compression.

σ	Normal stress = stress normal to shear plane
σ_v	Vertical stress.
σ_v'	Effective vertical stress = vertical stress less any pore water pressure. Important to the mechanics of the soil skeleton.
τ	Shear stress
τ_P	Peak or failure shear stress.
τ_R	Residual shear stress
ϕ_P, ϕ_P'	Angle of internal friction (or friction angle) at peak shear strength - particularly useful for noncohesive or silty soil. $\phi_P = \arctan {}^{\tau}/\sigma$.
ϕ_R, ϕ_R'	Same as above but for residual strength.
BI	Brittleness index = $\frac{\tau P - \tau R}{\tau P}$
PL	Plastic limit, % water dry basis
LL	Liquid limit, % water dry basis
PI	Plasticity index = LL - PL
CSH I	One type of tobermorite, $CaO\ SiO_2\ nH_2O$ using cement chemists terminology

Acknowledgments

The following people have contributed particularly to this work:

Russell Nye, Senior Research Technician
Michael Shaffron for Consolidation Data Reduction
Lindsay Patten, Student Chemist
Penny Hudson, Mineralogist
Paul Predecki, X-ray Diffraction
Ed Bates, EPA Cincinnati

I. INTRODUCTION AND SCOPE

A. Object

This Appendix presents a summary of work conducted under Contract 68-01-6487 and Cooperative Agreement CR809233. A more complete report including detailed descriptions of materials used, testing procedures, and results will be published upon completion of Cooperative Agreement CR809233. This work was undertaken to survey the possibility of use of spent oil shale itself in constructing a deeply buried liner below embankments of spent oil shale. Some possible modification of these spent oil shales were to be tried including the admixing of autoclave mellowed burned spent oil shale with the hope of reducing the cementation tendencies of otherwise rather fine grained material, sometimes of low emplaced permeability, and of reducing the permeability due to hydrothermal generation of clay like species. In general a material was sought which had much of the frictional characteristics and volume stability of silt but the impermeability of clay without a tendency for eventual cementation on the one hand or leachability and partial soil skeleton loss on the other.

One of the important needs of a spent oil shale based "clay" liner is low permeability. Perhaps the next most important is self healing ability if it risks being cracked through subsidence below or geologic faulting. A disadvantage of high strength soil such as can be achieved by cementation, dehydration or compaction is that, "once ruptured, the structure does not readily, if at all, reform. Weak bonds possess a certain capacity for self healing. . ." (Ingles 1968). A third requirement is volume stability or resistance to swelling and shrinking.

The present study has mostly been concerned with 100% standard and 100% modified proctor compacted specimens of spent oil shale although static compaction of some TOSCO II and Lurgi material to some 280 psi was done during torsion shear strength apparatus "shake down." The specimens have often seemed too brittle for good self healing due to high compaction and/or cementation. Their volume stability to consolidation under 280 psi pressure has been good, however.

Any detrimental effect of drying on the spent oil shale liner materials is presently speculation. There seems to be little shrinkage, in general, but the effect on permeability and self healing capability when re-wetted is unknown. The self healing capability while still dry is perhaps nill for some of the more cemented materials but lesser cemented materials such as TOSCO II material may show some ability to flow into tension cracks while dry under say 300 psi overburden vertical pressure.

Fortunately the underground environment of the liner will probably be moist on the country rock side of the liner and can be made moist on the spent shale embankment side.

An important possible hazard to be considered is that of increased pore water pressure in loosely compacted somewhat saturated liner due to shearing, chemical deflocculation due to permeate composition, or earthquake liquification. In a too impermeable liner, an increase in pore water pressure may not dissipate rapidly enough so that shear strength would drop due to reduced friction between soil skeleton particles as the effective normal stress is lowered. The liner might then become more like a grease than a liner allowing a spent shale embankment to slide.

Some specimens of the present study have been proctor hammer compacted so well that they apparently begin on the dense side of the critical volume line so they generally dilate at the beginning of shear. This should reduce pore pressure rather than increase it as shear occurs. Standard proctor TOSCO II spent shale cured for a short time shows no peak in the stress/strain curve and must begin above the critical volume line and although probably self healing to some degree might, in spite of its silty nature and high permeability, develop pore pressure during rapid shearing or other disturbance. These considerations have not been directly addressed in this study. Mainly plasticity and self healing problems in the face of cementation have been addressed.

Compressibility coefficients at various normal pressures in conventional oedometers have been determined on compacted specimens of zero age in looking for any collapse of the soil skeleton at higher pressures than even the 280 psi vertical pressure of the torsion tests. Of course the vigorous compaction used in preparing the specimens has reduced any tendency for collapse and pore pressure increase but study of wetting or saturating is also needed. Wetting has been tried for spring oedometer specimens after various aging times before determination of torsion shear strength and accompanied by specimen volume measurement before and after wetting during permeability testing.

B. Approach

The routine testing approach has centered around study of rather highly consolidated specimens of various mixtures of spent oil shale at two moisture contents, one at optimum water content for maximum dry density, the other at a somewhat wetter than optimum water content. Often wetter than optimum material is used for small dam cores and around abutments for increased flexibility and lower brittleness and sometimes lower permeability also results. A vertical consolidation pressure of around 280 psi was produced by spring loaded oedometers.

To simulate a liner placement technique sometimes proposed, the specimens were compacted in spring oedometer sheaths to 100% of standard proctor or 100% of modified proctor. These compactions allowed a small further consolidation in the oedometers. The oedometer consolidation is a sort of model of burial under an embankment of moderate height and allows a standard and somewhat realistic environment for subsequent aging/curing/and or cementation processes in the specimen. There is some unreality in immediate application of the full 280 psi consolidation pressure just after compaction however, as some time is needed for construction of full embankment height.

After permeability testing a specimen, it was transferred from the spring oedometer to a rubber membrane in a triaxial chamber for torsion testing under a confining water pressure generally corresponding to an assumed K_o of 0.5 to 0.7. A K_o of 0.7 is higher than corresponds to a two dimensionally normally consolidated silty material but may be about right for certain specimens. In this way the tendency for swelling in diameter of a specimen as it in effect is extruded from the oedometer sheath to the rubber membrane in the triaxial chamber is mitigated. Such swelling might break cementation of cemented specimens. Without the confining pressure even some stiff somewhat cemented specimens were crushed when only moderate vertical pressures were applied prior to torquing.

It is desirable to perform shear strength tests on undisturbed specimens. Specimens may be disturbed by swelling which softens them, by overconsolidation which during extrusion hardens them or by breaking cementation which softens them or fractures them prematurely. After obtaining the torsion stress/strain curve, the specimens were removed from the triaxial container and their enclosing gum rubber membranes cut away so previously transferred longitudinal acrylic paint stripes on the specimens could be examined and the specimen photographed.

Some physical and chemical properties of the specimens were next determined on dried fragments left from the torsion test. These include EGA analysis for hydrate water of species formed during curing. Some of these species are of a cementing or potentially leachable nature. X-ray diffraction scans for confirmation or identification of these species were also made.

The Atterberg limits of beginning materials and blends of spent shale materials are a parameter important in soil mechanics correlations. These were obtained for some raw material spent shale and mellowed spent shale. Atterberg limits on cemented specimens were not made.

Considerable time was needed to learn how to best operate the specially built triaxial torsion machine. Some specimens from preliminary series were tested under various confining water pressures and with different variations of specimen extrusion methods before the combination of conditions used for most of the specimens prepared for the following experimental plan was standardized. At the beginning it was believed that cured specimens containing much of the burned TOSCO spent shale would be too cemented to be handled by the triaxial torsion apparatus and this material was limited to 30% in mixtures with less cementing TOSCO II material. This fear was validated as tests proceeded. Some of the 30% mixtures were strong enough to cause slipping of the piston rod in the torque transmitting collet gripping it. Usually this could be remedied by further tightening of the collet. Also sometimes a little bending over of the brass vanes in the pore stones gripping a well cemented specimen occurred during twisting.

It was also feared that there might be poor contact and gripping of the top of the specimen by the piston pore stone when standard proctor and particularly when modified proctor compaction was used, especially since a 3/32 inch cross section rubber o-ring was being used at the periphery of the piston pore stone between the specimen and stone. Preliminary experiments using a pneumatic loaded oedometer with proctored material seemed to partially support this fear and many of the main series of specimens were loaded in the spring oedometers using the o-rings but with some loose material sprinkled on top of the compacted specimen within the o-ring before insertion of the piston and application of spring pressure. Previous static compactions with the spring alone without proctor compaction had shown attainment of rather high density although not as high as by some standard proctorings and all modified proctorings. For this reason some hope was held that the thin loose layer would bond well enough to the piston pore stone-vane structure. When torsion tests were made, however, it was found that slippage often occurred between specimen top and the piston pore stone without involvement of the interior of the specimen to much extent. Moreover disassembly of the specimen and porestones after torsion testing revealed that the material at the top of the specimen was much softer than that at the bottom and should not be expected to be as strong.

Immediately a new procedure of torsion testing was devised wherein the vertical pressure on the specimen was brought up to that originally existing during consolidation in the spring oedometer with the hope that this could dig the vanes into the top of the specimen and secure a good enough grip. This was somewhat successful. The vertical pressure on the specimen during torsion testing should probably be kept at that during consolidation anyway for less likelyhood of disturbance of the specimen. With fixed upper and lower specimen porestones about 1/2 of the vertical pressure is lost during extrusion of the specimen in the triaxial confining chamber and should be replaced before torsion. As this fraction was apparently unaffected by elimination of the loose layer and piston porestone o-rings in a revised specimen loading procedure some other reasons for the loss have been sought.

Loss of vertical pressure on the soil skeleton during unsheathing is presently believed to be due to (1) some back lash in the pedestal pins and mating sheath holes and (2) some specimen overconsolidation caused by excess piston pressure on the specimen generated by friction drag between the teflon coated sheath and the specimen. As the results of the effect are apparently of little consequence at the present rough stage of development of the method and useful correlations and comparisons between specimens were being made a further change in methodology was not instituted. One change might be to grease the inside of the oedometer sheath contacted by the specimen but this would make temporary adherence of the acrylic paint marker stripes difficult.

C. Experimental Plan and Independent Variables Used

Table B-I 1 summarizes the experimental plan. Each box under columns C1 and C2 represents one specimen compacted in a spring oedometer and consolidated at around 280 psi. Duplicate specimens compacted in a three segment ring mold were also prepared then coated with wax for curing at constant moisture prior to being subjected to the Brazil indirect tensile test. These Brazil test specimens are denoted by "B" in the boxes under columns C1 and C2.

The boxes under the C3 columns which have entries represent specimens prepared by standard proctor compaction and tests by pneumatic arm oedometer

TABLE B-I 1 Experimental Design - TOSCO II, Lurgi, and Mixtures of mellowed TOSCO and Mellowed Lurgi With Burned and Unburned TOSCO And Unmellowed Lurgi Spent Shale

Material	Later Satd.?	Spring Oedometer and Triaxial Torsion Tests						Pneumatic Arm Oedometer C_3 = Standard Proc. except with * which is Modified Proc.				
		C1 = Modified Proc.			C2 = Standard Proc.							
		T1	T2	T3	T1	T2						
Unburned TOSCO II	Yes+	22% 54 B	22% 34 B	22% 46 B	25% 71 B	25% 32 B		* 22% H_2O	25%	20%	30%	
	No	22% 55**	22% 35	22% 47	25% 91	25% 33						
10% Burned TOSCO, 90% Unburned TOSCO II	Yes+	23 56 B	23% 39 B	23% 48 B	27% 70 B	27% 31 B		* 23%	* 28%	22%	27%	33%
	No	23% 57**	23% 49		27% 90	27% 30						
	Ample Moisture+	28% 53 B	28% 62 B									
20% Burned Tosco 80% Unburned TOSCO II	Yes+	24% 75 B	24% 60 B	36 B	24% 80 B	24% 37 B		* 24%	* 29%	24%	29%	34%
	No	24% 67	24% 63		24% 81	24% 38						
	Ample Moisture+	29% 66 B	29% 61 B									
30% Burned TOSCO 70% Unburned TOSCO II	Yes+	25% 76 B	25% 58 B	25% 40 B	28% 89 B	28% 41 B		* 25%	* 34%	28%	33%	39%
	NO	25% 77	25% 68		28% 88	28% 42						
	Ample Moisture+	34% 74	34% 59									
Ample Moisture 75% Mellowed Burned TOSCO, 25% Burned	Yes+	55% 92 B	55% 86 B					* 55%				
50% Mellowed Burned TOSCO, 50% TOSCO II Ample Moisture	Yes+	40% 93 B	40% 87 B					* 40%	45			
Lurgi	Yes+	22% 51 B	22% 72 B	22% 43 B	30% 78 B	30% 64 B		* 22%	* 27%	30%	35%	40%
	No	22% 50	22% 73	22% 44	30% 79	30% 65						
	Ample Moisture+	27% 52 B	27% 69 B	27% 45 B								
75% Mellowed Lurgi 25% Unmellowed Ample Moisture	Yes+	25% 82 B	25% 83 B					* 25%	25	30	35	
50% Mellowed Lurgi 50% Unmellowed	Yes+	25% 84 B	25% 85 B					* 25%	25	30	35	

* Modified Proctor

\+ Permeability determined also

**Permeability determined out of order resulting in "yes" instead of "No" later saturation.

at five consolidation pressures up to 310 psi. The water contents chosen were those for optimum moisture for maximum dry density for standard and modified proctor and several water contents including some wetter than optimum for standard proctor, four or five water contents total, for each of the nine spent shale raw material types or mixtures tests by the other methods . The loading number for the spring oedometer experiments is given in the lower left corner of each applicable box in Table B-I 1. This number is followed by B if Brazil tests specimens were to also be prepared. The water to be added, percent dry basis, in preparing the specimens is entered in the upper area of each box.

C1 represents modified proctor compaction, C2 standard proctor compaction. T1, T2, and T3 represent curing times of nominally 2, 4, and 8 weeks respectively. "Yes" represents that later "saturation" was to be carried out by means of permeability measurement operations, "No" represents that the spring oedometer specimen was to be torsion tested without saturation after consolidation and before torsion testing.

II. DISCUSSION OF RESULTS

A. Permeability

Permeability coefficients were more reproducible and self consistent than expected. Perhaps the high consolidation pressure (280 psi) contributed to minimum channeling along the wall of the oedometer sheath as well as to minimizing flow between peds of soil fabric which may produce variable permeabilities at lower vertical pressures. Also bimodal permeation channel development may be minimized by the compaction at optimum water content often used in producing these specimens.

During mixing of material wetter than optimum, granulation occurred in which pellets of material formed which seemed to be wetter on their surface than inside. This seeming tendency toward synergesis probably disappears as mineral hydrates form during curing but during compaction and initial consolidation the wet surface of the granules may allow smearing of their surfaces with development of parallel alignment of any clay-like mineral platelets present during compaction by proctor hammer. This may account for some of the observed lower permeability at wetter than optimum moisture content compared to a dryer moisture content.

Reduced permeability for compacted specimens of most spent shales at wetter than optimum moisture content was observed. Figure B-II 1 shows this effect for both standard and modified proctored specimens made from mixtures of burned TOSCO and unburned TOSCO II spent shale. However, the effect is weak or nil for 100% unburned TOSCO II material, at four weeks curing time. Of course some other factor may be influential with these cementing materials such as increased hydrate formation at higher water contents.

Figures B-II 2, 3, 4, 5, 6, and 7 show a general but not universal mild downward trend of permeability at increasing curing times, especially beyond 30 days with the exception of the more cementaceous 70% TOSCO II with 30% burned TOSCO blend and the Lurgi spent shale which showed increased permeabilities beyond 30 days even though the latter had shown a decrease up to 30 days. The lower permeability at wetter than optimum water content is evident again with the Lurgi material in Figure B-II 6 when the 22% water added is compared with the 27% water added curves within the modified proctor constraint (square data points).

It is difficult to make sense of the sketchy permeability vs curing time curves of Figures B-II 2, 3, 4, 5 and 6. This is perhaps caused by the irregular course of mineral hydrate formation and disappearance as curing time increases. Reduction of the mineral grain density (determined by the Beckman air pycnometer) of pulverized 48°C oven dried material from the torsion test is assumed to be an indication of the extent of hydrate water incorporated in cementaceous and/or bulk producing species in the specimen. Figures B-II 8, 9, 10, 11, and 12 plot the remarkable course of the extent of hydrate water present in the specimens after torsion testing as indicated by mineral grain density. If a lower mineral grain density indicates more mineral hydrate water there is an appreciable maximum in mineral hydrate

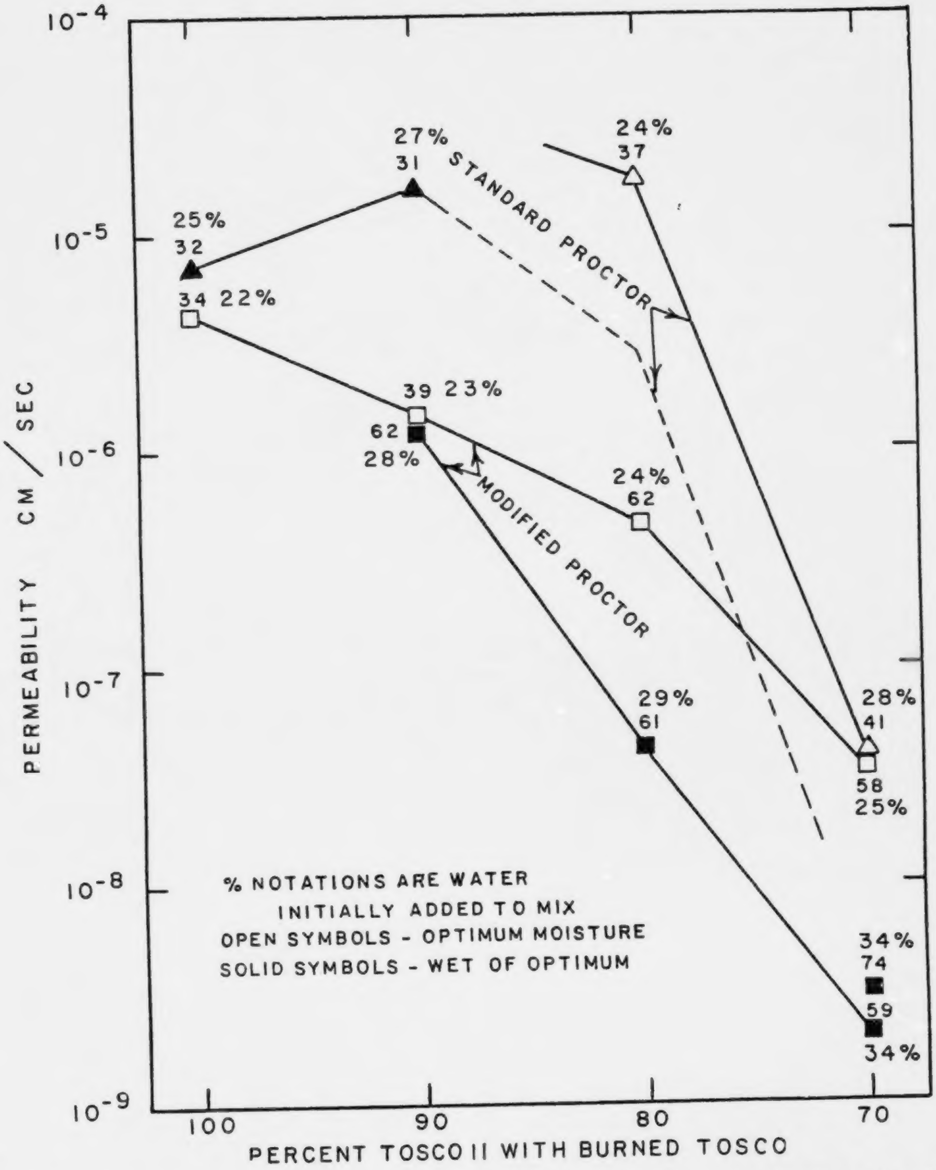


Figure B-II 1. Permeability of Mixtures of Burned TOSCO And Unburned TOSCO Spent Shale After Approximately Four Weeks Curing in Spring Oedometers.

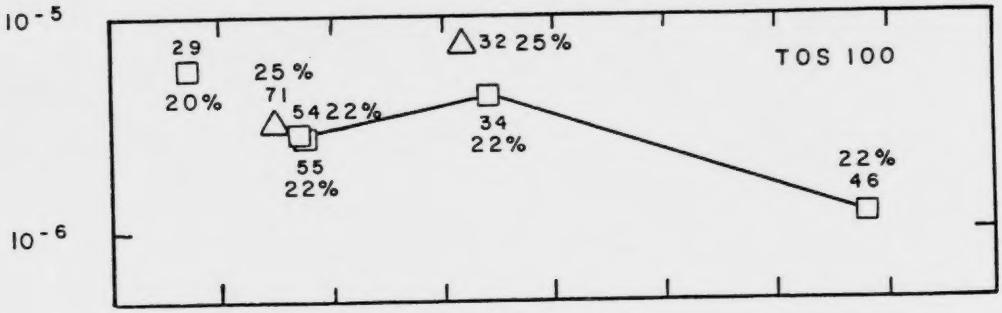


Figure B-II 2. Permeability of 100% TOSCO II Spent Shale (TOSCO 100)

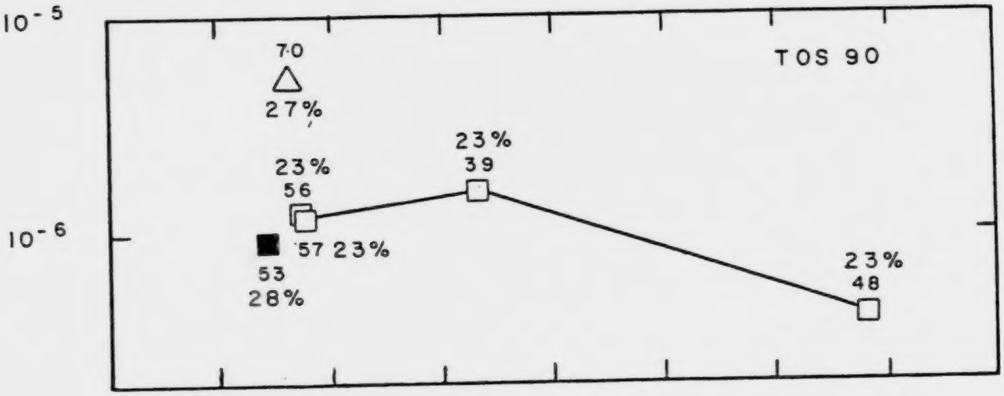


Figure B-II 3. Permeability of 90% TOSCO II - 10% Burned TOSCO Spent Shale (TOSCO 90)

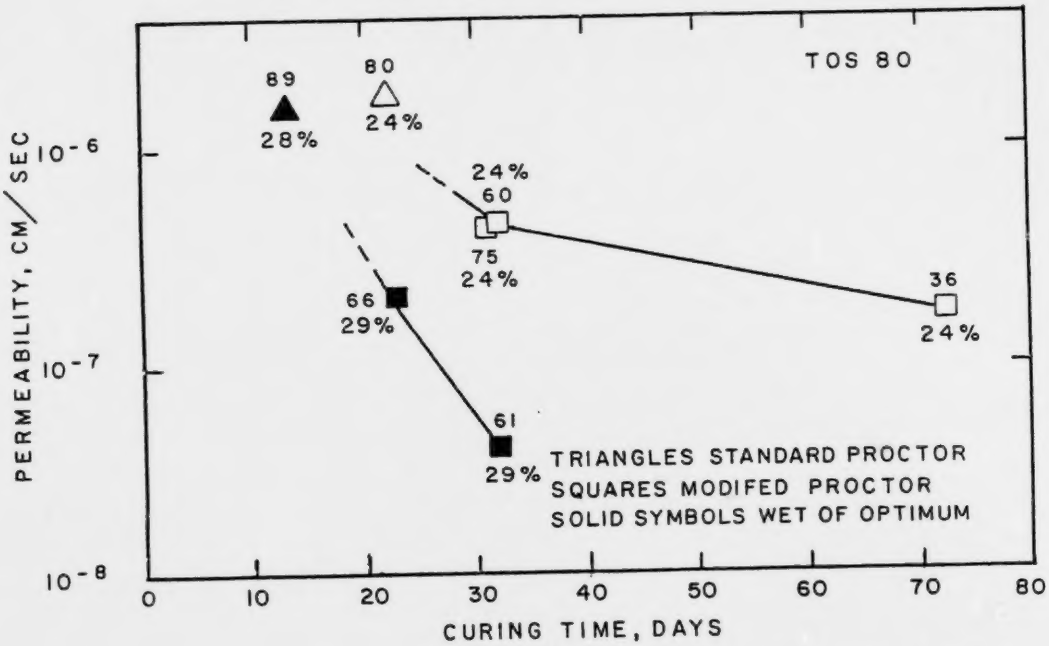


Figure B-II 4. Permeability of 80% TOSCO II - 20% Burned TOSCO Spent Shale (TOSCO 80)

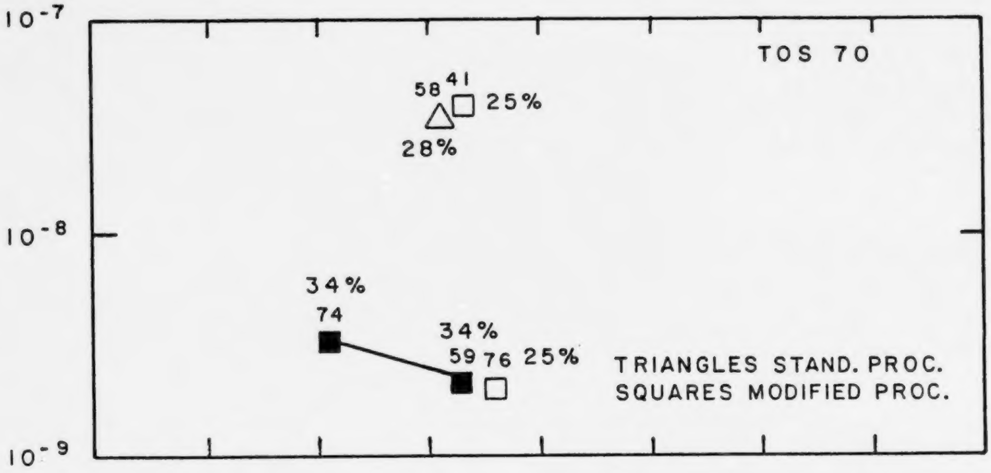


Figure B-II 5. Permeability of 70% TOSCO II - 30% Burned TOSCO Spent Shale (TOSCO 70)

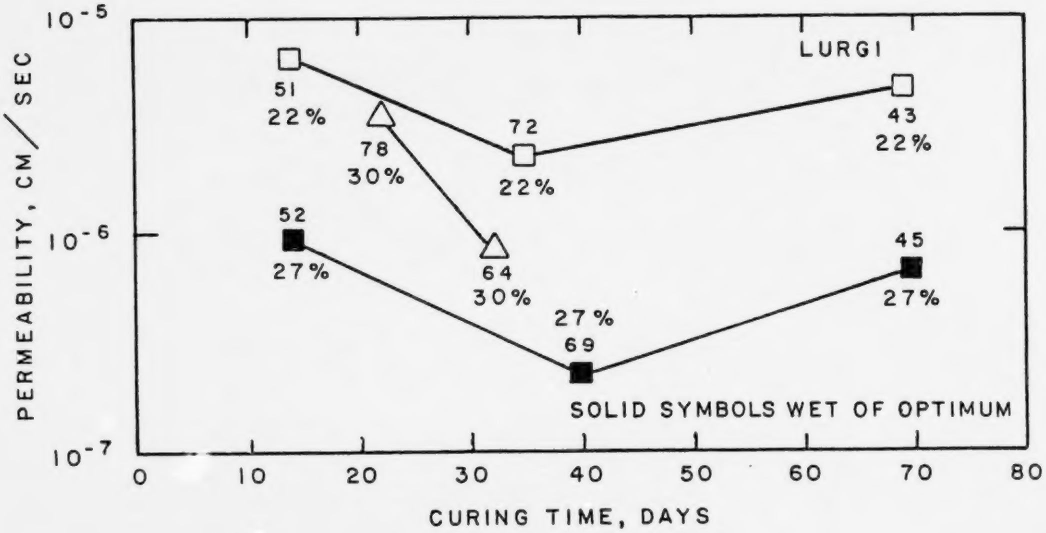


Figure B-II 6. Permeability of Lurgi Spent Shale

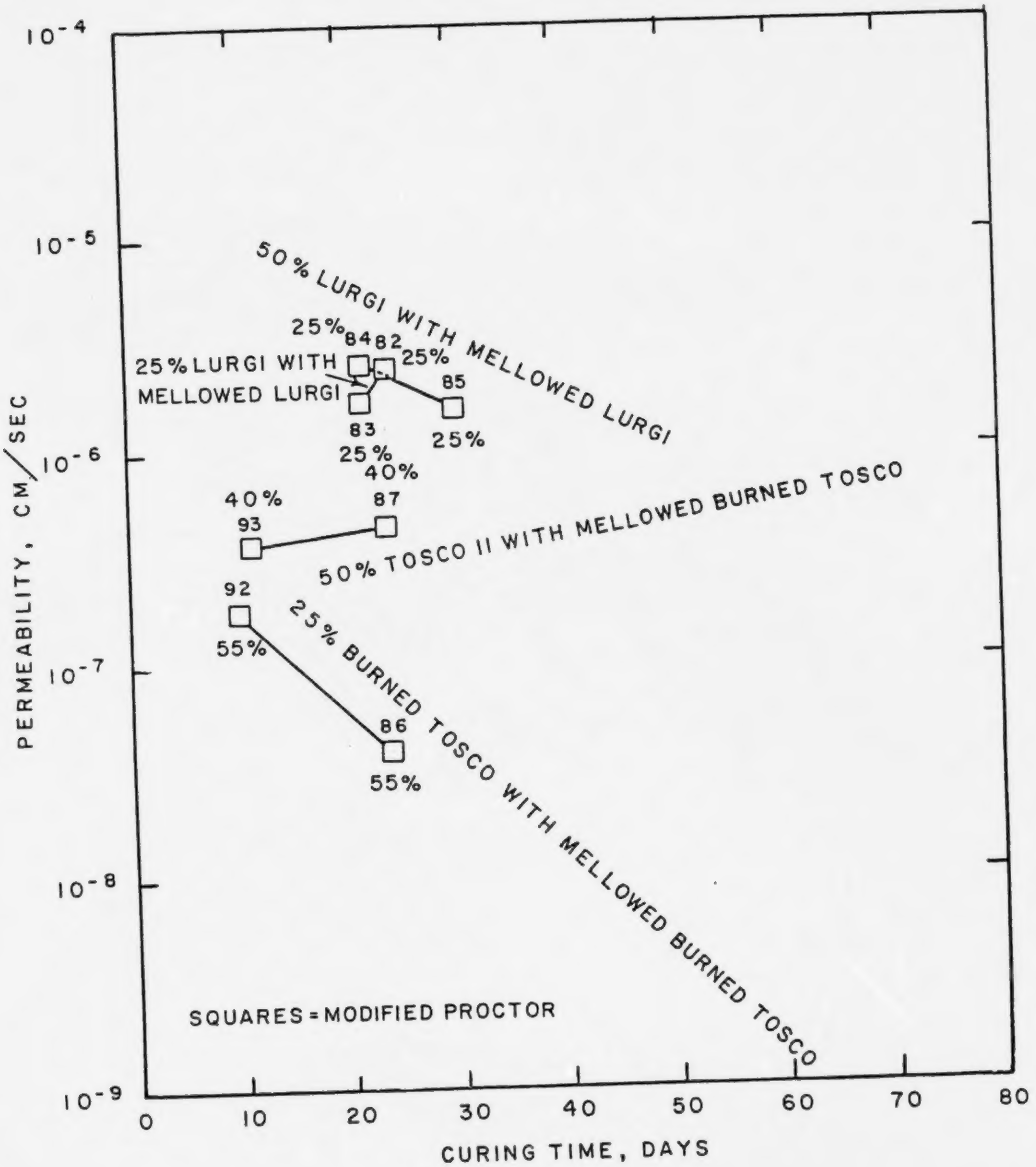


Figure B-II 7. Permeability of Mellowed Lurgi (M14) Mixed into Lurgi and Mellowed Burned TOSCO (M-15) Mixed into TOSCO II and into Burned TOSCO Spent Shale

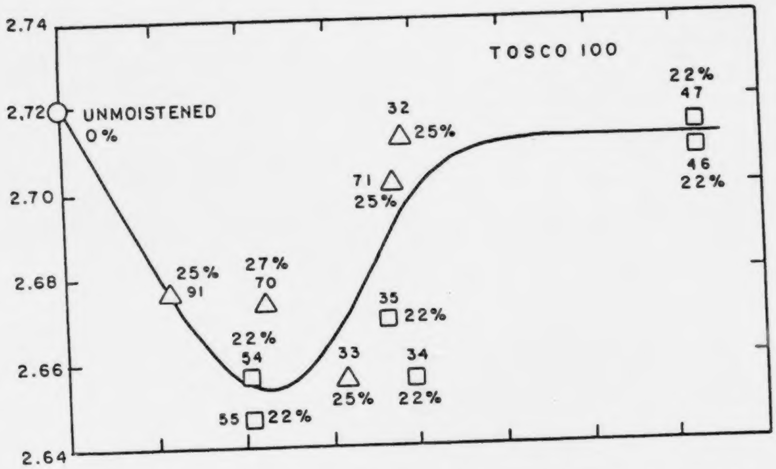


Figure B-II 8. Mineral Grain Density vs Time for TOSCO 100 Spent Shale

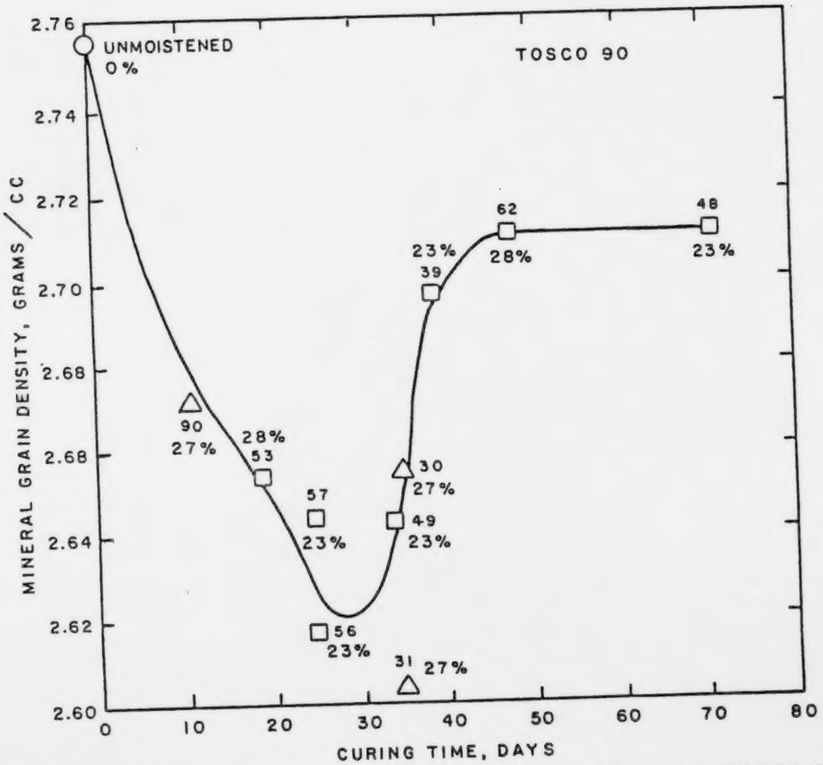


Figure B-II 9. Mineral Grain Density vs Time for TOSCO 90 Spent Shale

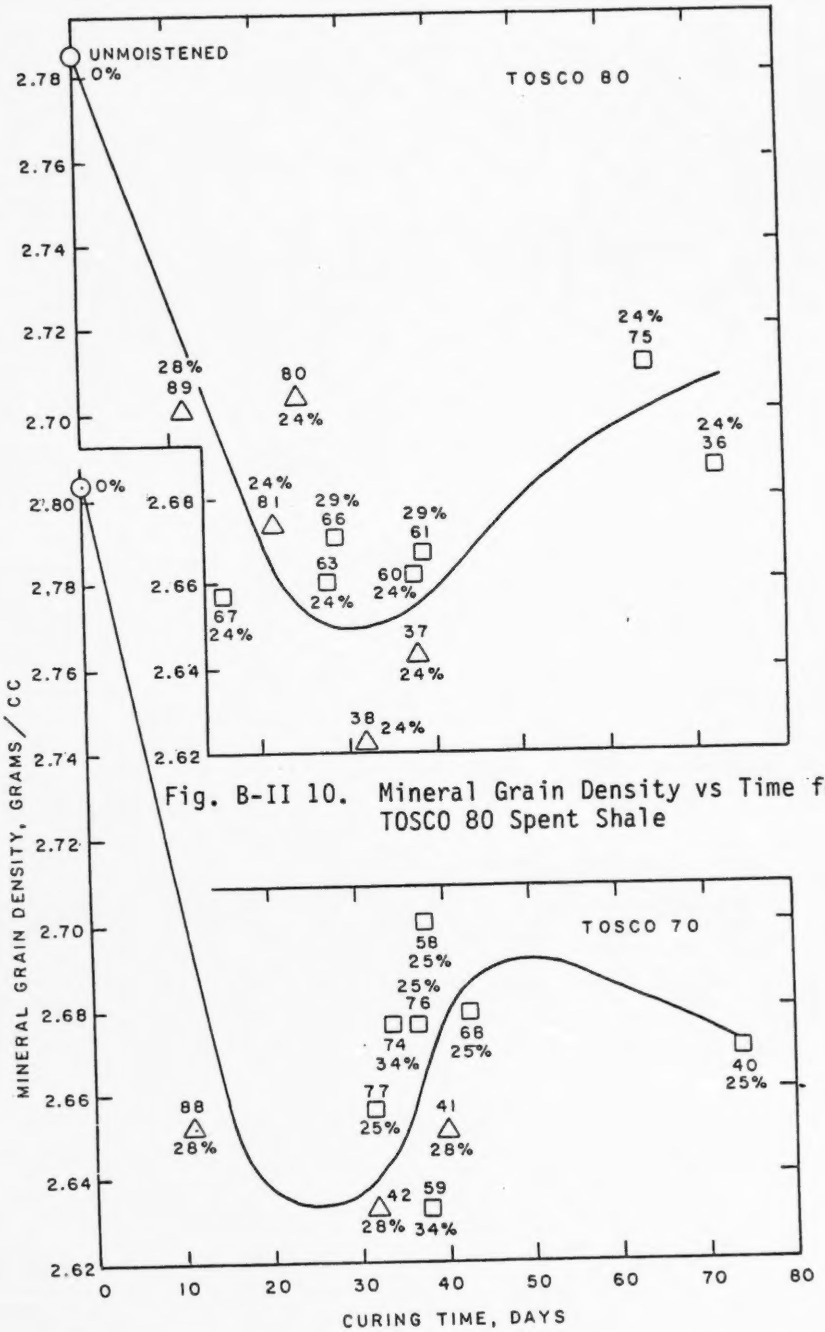


Fig. B-II 10. Mineral Grain Density vs Time for TOSCO 80 Spent Shale

Figure B-II 11. Mineral Grain Density vs Time for TOSCO 70 Spent Shale

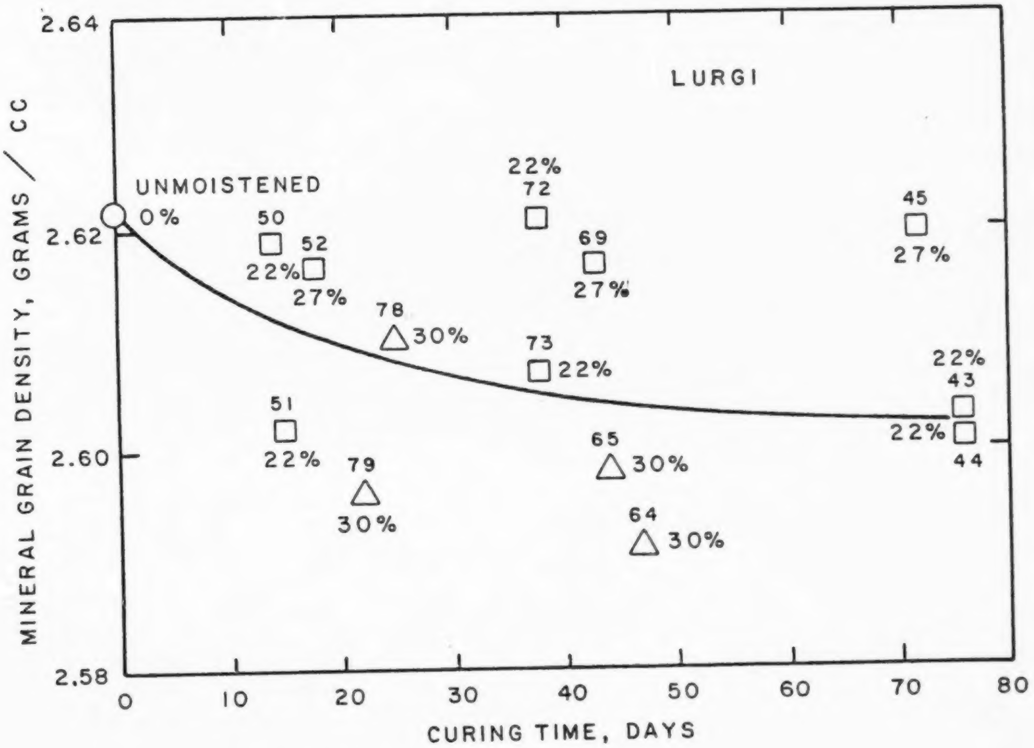


Figure B-II 12. Mineral Grain Density vs Time for Lurgi Spent Shale water at around 20-30 days as curing progresses with time for all unmellowed TOSCO spent shale materials studied including unburned TOSCO II spent shale.

The Lurgi spent shale, however, showed not only less reduction in mineral grain density after curing compared to the grain density of the uncured dry raw material but no clear cut minimum and some scatter of the data points. Apparently a different cementation mechanism is involved with the Lurgi material than with the TOSCO materials or else the Lurgi pilot plant pre-hydrated the material to considerable extent during post pyrolysis operations.

The interpretation of the minimum in the mineral grain density plots of the TOSCO spent shales (Figures B-II 8, 9, 10, and 11) as due to mineral hydrate maxima is substantiated by Figure B-II 5, introduced later, which shows maxima in a low temperature evolved gas analysis water peak (at approximately 150^oC) at curing times corresponding to the minima in mineral grain density. This peak appears to be due to a tobermorite-like species, CSH I ($CaO\ S_1O_2\ nH_2O$) and ettringite.

Figure B-II 13, shows the permeabilities found for autoclave mellowed Lurgi (autoclave run M 14) mixtures with Lurgi, an autoclaved burned TOSCO (M15) mixture with unburned TOSCO II and an autoclaved burned TOSCO (M15) mixture with burned TOSCO spent shale plotted vs void ratio e for certain of the spring oedometer specimens. These were all modified proctor specimens and the water added and curing times are noted by the data points plotted. The low permeability of the 75% autoclave mellowed burned TOSCO spent shale mixed with 25% of burned TOSCO spent shale is to be particularly noted in view of its low cementation to the time curing was stopped. Before concluding that the mixtures containing burned TOSCO spent shale giving the lowest permeability are most desirable in a liner the brittleness of the liner must be considered and also its ability to self heal after fracture or during tension movement.

The permeabilities were determined just before torsion testing, the void ratios were based on mineral grain densities determined on 48^oC oven dried material after torsion testing and bulk dry density of the specimens just after loading in the spring oedometers. The bulk dry density was calculated based on water added to the wet mixture loaded into the oedometer.

Figure B-II 13 shows that in general the greater the fraction of burned TOSCO spent shale that is blended into the unburned TOSCO II spent shale the less the permeability at a given void ratio. Lower void ratios give lower permeabilities also, however, as is the well known trend for ordinary soils. Fairly clearly the hydrate forming cementation reactions of burned TOSCO containing spent shale reduce permeability beyond that to be expected by simple reduction of void ratio determined using mineral grain density. This may be due to deposition of fine precipitate or gel within the spent shale particles interstitial spaces or it may be due to deposition at spent shale particle contacts that grows to invade the interstitial spaces. Growth of cementaceous hydrates within a given porous spent shale particle should not influence permeability of the specimen much.

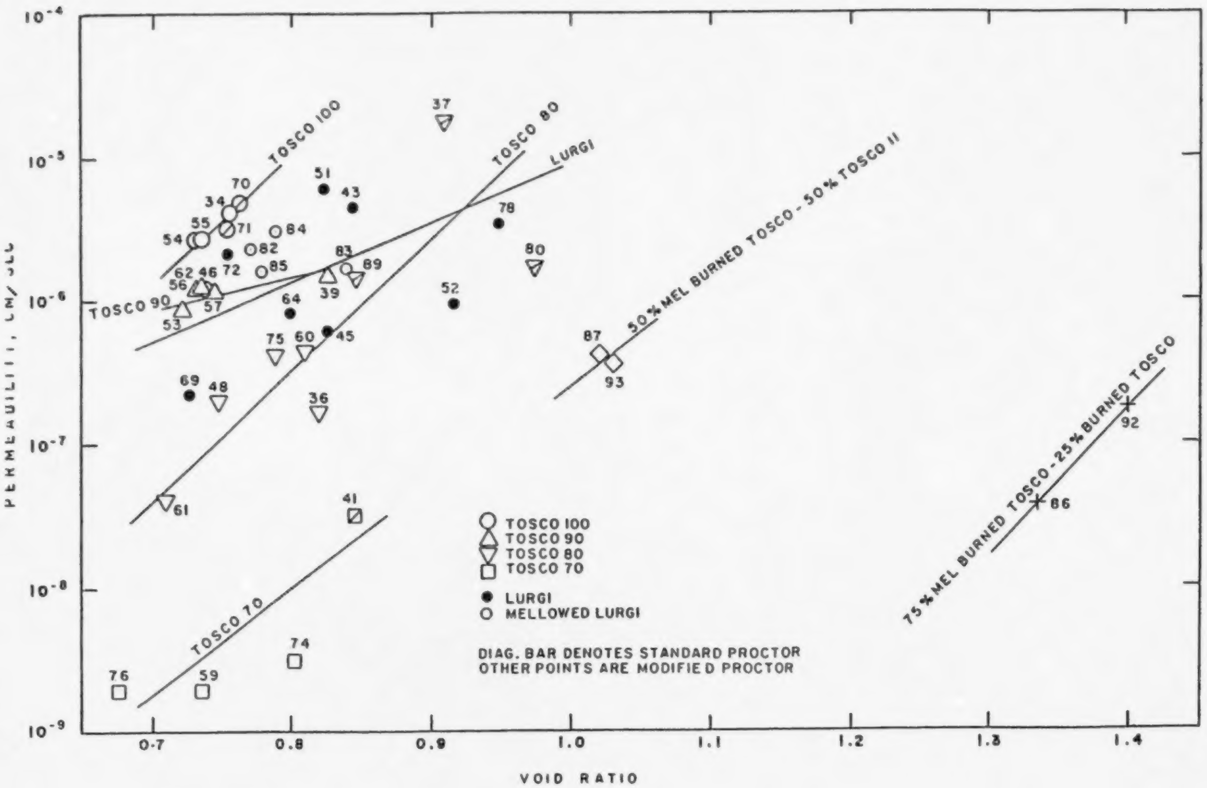


Figure B-II 13. Permeability of Spent Shales Correlated with Void Ratio

B. Peak Angle of Internal Friction $\emptyset_P$ Related to Self Healing and Its Trade off with Permeability

Figure B-II 14 shows a dilemma in trying to compound a liner material made from any mixture made from burned TOSCO and unburned TOSCO II spent oil shale. Both low permeabilities and low peak friction angles are desirable but they seem to be nearly mutually exclusive. A low friction angle allows easier or more extensive rapidly self healing. A high peak friction angle is shown by the more cemented specimens.

The peak angle of internal friction plotted in Figure B-II 14 is more easily reduced from the torsion data than a normalized peak shear strength. Also O_p may be directly used in one model of the rapid self healing process.

For a silty material (as many of the specimens here studied are) the torsion shear strength measurements give shear strengths proportional to the normal pressure on the failure plane (which is practically the same as the vertical pressure on the specimen). This is because the specimens are small enough so relief of pore pressure of a silty material is rapid and also because cementation in these specimens is nil. For such specimens in such a test that is not too quickly performed the peak shear strength and residual shear strength data obtained at known vertical pressure can be reduced to $\emptyset_P$ and $\emptyset_R$ respectively.

Many of the peak friction angles of the more cemented specimens measured are not as high as they should be because the looser, less compacted, specimen material near the top pore stone tends to fail before the more representative center of the specimen. Thus the dilemma in trying to attain low cementation as well as low permeability is probably more serious than even indicated by Figure B-II 14. Also probably few if any of the peak friction angles determined by the present torsion apparatus are as high as they should be for the more cemented specimens due to eccentricity of the rotating piston and top pore stone and vanes due to any non trueness or bowing of the piston rods which can cause development of much side thrust without registering of much torque. This would be an insignificant factor, however, with a soft specimen which can deflect to accommodate a little side thrust with no rupture.

The curve of Figure B-II 15, permeability vs peak friction angle, for the Lurgi spent shale seems to run counter to the curve of Figure B-II 14 for TOSCO spent shales. There appears to be a difference in the materials causing for the Lurgi a reduced permeability with reduced angle but for TOSCO materials an increased permeability with reduced angle. For TOSCO spent shale of Figure B-II 14 less cementaceous species seem to be the cause of low friction angles but for Lurgi spent shale of Figure B-II 15 greater water content may be operative, at least at the short curing times involved. With the fast setting TOSCO mixtures perhaps the water contents role in softening a material is overshadowed by rapid cementation. With longer curing times perhaps the slow setting Lurgi material would more resemble the TOSCO mixtures in its permeability vs friction angle plot.

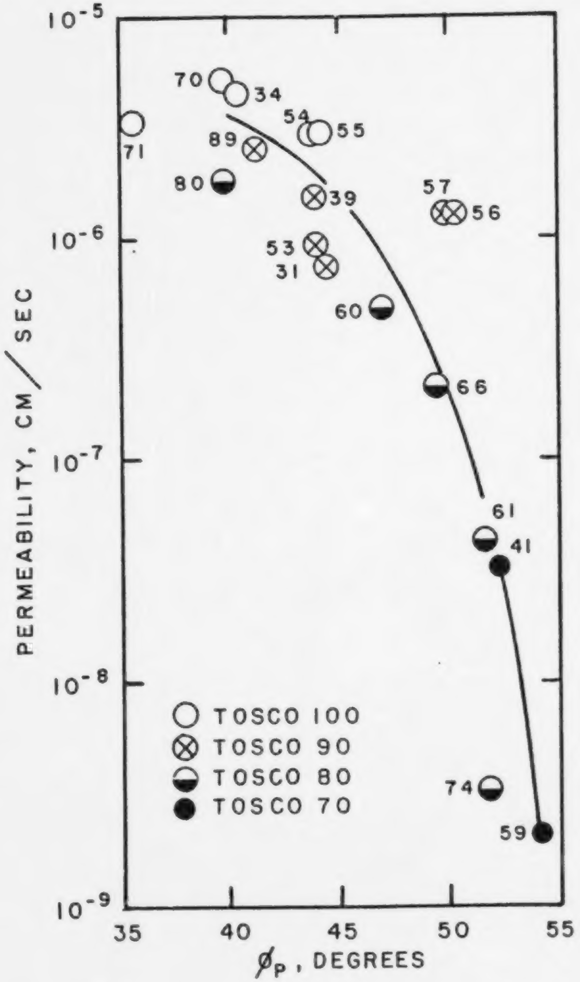


Figure B-II 14. Permeability of TOSCO Spent Shale Mixtures Correlated with Peak Friction Angle.

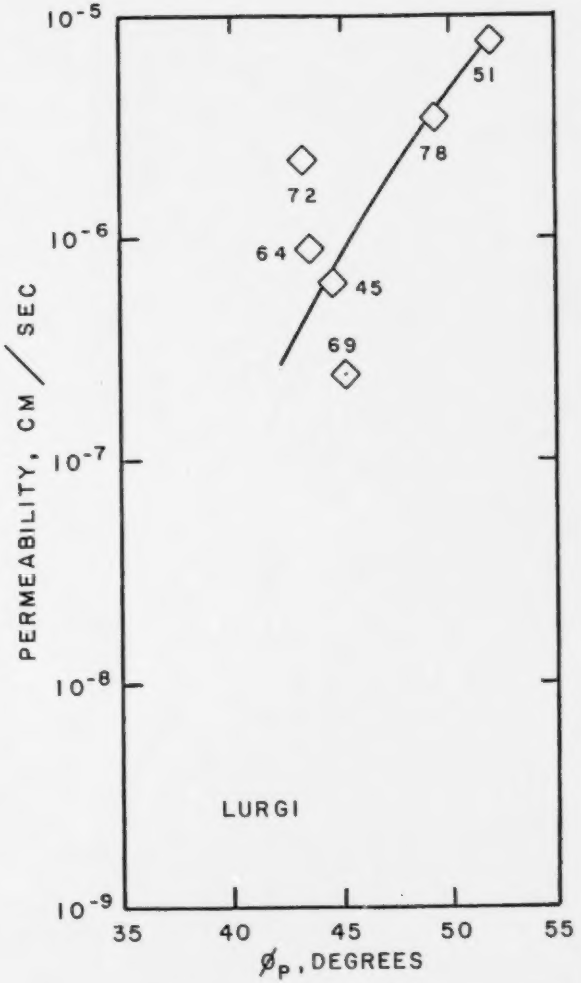


Figure B-II 15. Permeability of Lurgi Spent Shale Correlated with Peak Friction Angle.

C. Residual Shear Strength and Critical Void Ratio Related to Slope Stability

Data obtained as ϕ_P and ϕ_R can be used in a soil mechanics model where drainage of pore pressure is rapid. Drainage of pore pressure in the field is relatively rapid, even for a thick liner layer, if rate of shear is relatively slow. However if pore pressure drainage is not rapid a more complicated and hazardous case must be considered.

Before the liner shears and therefore before the soil skeleton in the shear zone might be compressed (if its void ratio is above the "critical void ratio" for the material) the peak shear strength may be used to estimate the maximum angle of inclination of a liner below a spent shale pile before the pile will slide through shear failure in the liner parallel to the weak liner. But if the liner does begin to shear at some place due to the peak strength being locally exceeded and if the liner material does contract during shear (the "critical void ratio" of the shearing liner being lower than the emplaced liner void ratio) and if pore water pressure can build up in the plane or zone of failure trouble is probable. Pore pressure will reduce the effective vertical pressure σ_v' and reduce the effective peak shear strength τ_P' of the section of liner beginning to shear. The reduced strength of the initially shearing section and the strain occurring shifts the stress toward the remaining intact section of liner and its strength may also be exceeded. Thus a "progressive failure" occurs which results in a slide.

The most conservative design strengthwise (and possibly the most expensive) is (1) to design using the weak strength developed after shearing occurs with no drainage where the effective normal stress σ' is reduced and τ' is also reduced (since $\tau = \sigma' \cos \phi$) or (2) to design with the low residual shear strength τ_R which is developed as the thrust of the failure shear plane increases (and any cementation or particle to particle interlocking is broken and any clayish mineral species platelets are aligned parallel to the plane thus producing a more slippery shear plane), whichever is lowest. It was beyond the scope of this present work to test the true residual shear strength of the many materials and conditions of emplacement ring shear apparatus.

The change in void ratio from emplaced void ratio to the critical void ratio at failure has not been measured in the torsion apparatus used in this study. Probably it is best measured (for plastic specimens) in a conventional "triaxial" soil testing apparatus in which the volume of the specimen can be measured throughout a test. Attempts to make this measurement on cemented specimens will probably be futile, however. It should be done on good candidate (non cementing) liner materials. The change in void ratio at critical conditions (where shearing, particularly simple shearing, has caused the specimen to reach a steady state) helps determine the pore pressure during failure and its degree of influence on the shear strength during failure.

D. Brittleness Index Related to Cementation and Permeability

In calculating the brittleness index two shear strength values τ_p and τ_R must be not only be normalized to the same vertical pressure but good, $\emptyset_p$ and $\emptyset_R$ data is needed as a working number is derived from the difference between two large numbers. This decreases the chances for a good brittleness index, BI, result compared to those for a good $\emptyset_p$. This is believed to be one reason correlations using $\emptyset_p$ show less scatter than those using the brittleness index. On the other hand this is not a substitute for BI which is retained in spite of its imprecision for certain illuminating correlations.

Figure B-II 16 is a comparison of BI and $\emptyset_p$ for Lurgi, TOSCO, and the mixtures involving mellowed material.

Figure B-II 17 is a plot of permeability vs brittleness index of specimens made from TOSCO 70, TOSCO 80, TOSCO 90, TOSCO 100 mixtures containing mellowed materials, and Lurgi spent shale raw materials. Difficulty in selecting materials giving both low permeability and low brittleness index from materials giving curves on the right of the plot is evident. Some materials of the curve on the left of the plot are, on this basis, perhaps acceptable for a liner, however. These materials give a negative brittleness index calculated from the quick torsion shear strengths $\emptyset_p$ and $\emptyset_R$.

The cause of a negative brittleness index seems to lie in low permeability along with neglegible cementation. Low permeability of a specimen in the torsion test is believed to prevent rapid drainage at the beginning of torsion with development of appreciable positive pore pressure as specimen distortion and contraction occurs which reduces the effective vertical stress σ_v. As twist procedes the excess pore pressure drains and σ_v increases causing τ to rise. The result is an increasing torque vs time plot on the x-y recorder of the torsion test machine.

For screening candidate liner materials the ability of the torsion test to indicate low permeability, non-cemented, simple shearing materials seems useful. Whether the added ability of the torsion tester to transfer consolidating curing specimens from oedometer to torsion tester without much sample disturbance is essential is perhaps debatable. It seems, however, that every opportunity should be given the specimen to demonstrate any small extent of cementation it has achieved during aging. Disturbance would tend to break the cementation before testing thus reducing the peak of the torsion stress strain curve.

E. Relation of Peak Friction Angle $\emptyset_p$ and Brittleness Index BI with Initial Torsional Stiffness and Shear Modulus G

Figure B-II 18 is a correlation of peak friction angle $\emptyset_p$ with simple shear modulus G obtained from the initial torsional stiffness, derived from volts/degree twist on the stress strain plot. There seems to be a higher curve for brittle material and a lower curve for soft material.

In comparing these G's with others the increase of G with confining stress (some 280 psi σ_v usually existed here) must be remembered. Some of

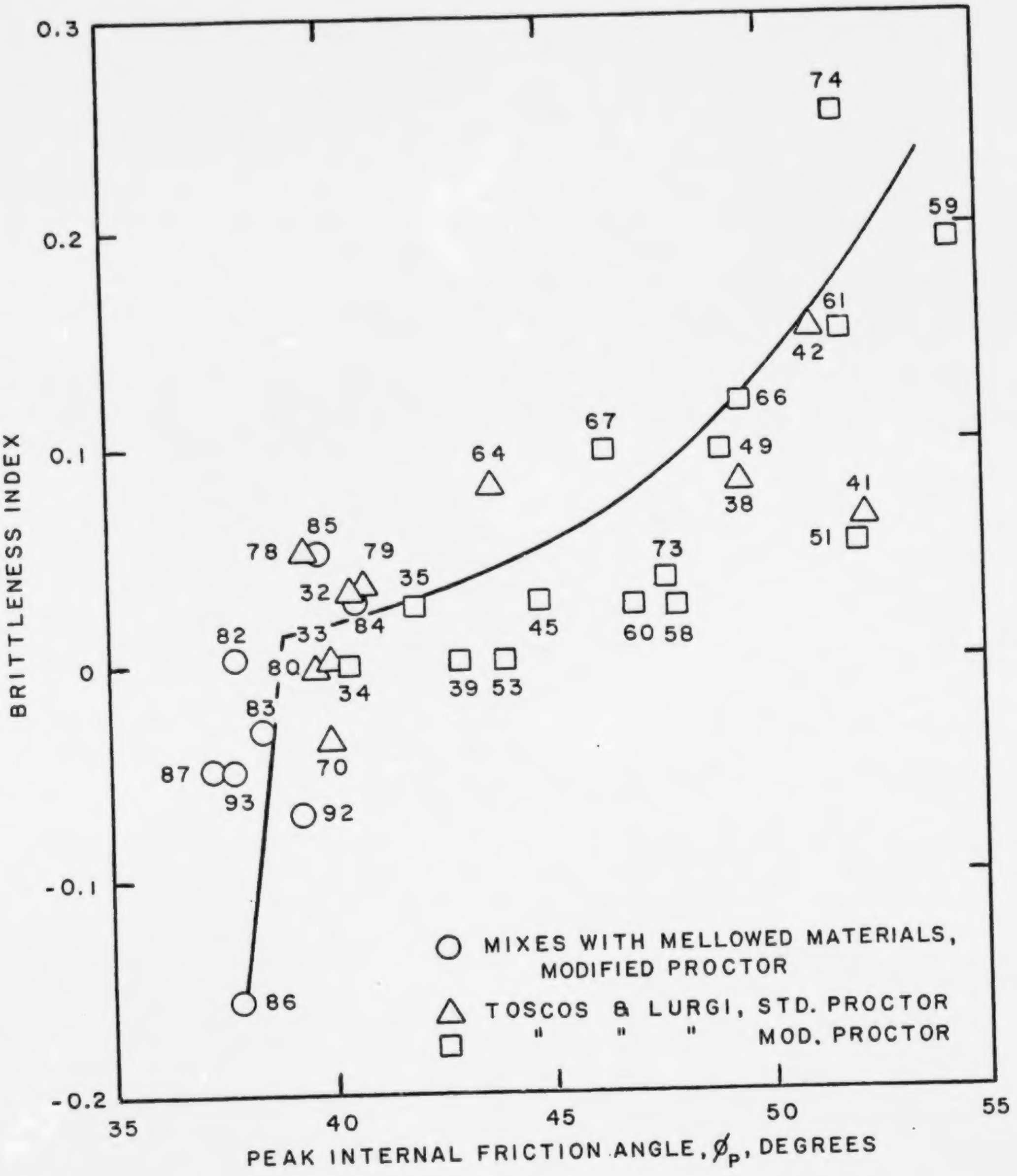


Figure B-II 16. Brittleness Index Correlated with Peak Friction Angle.

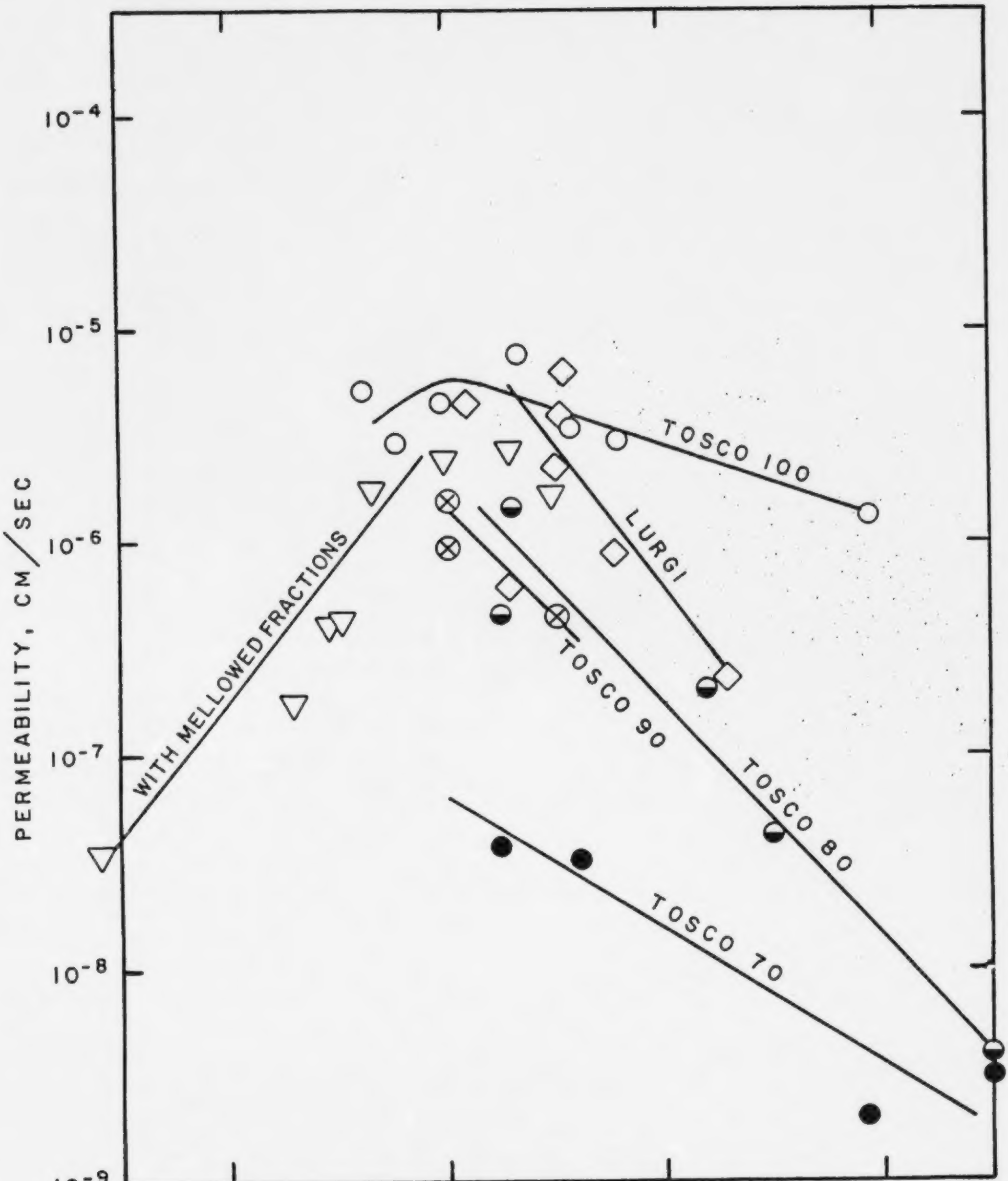


Figure B-II 17. Permeability Compared with Brittleness Index

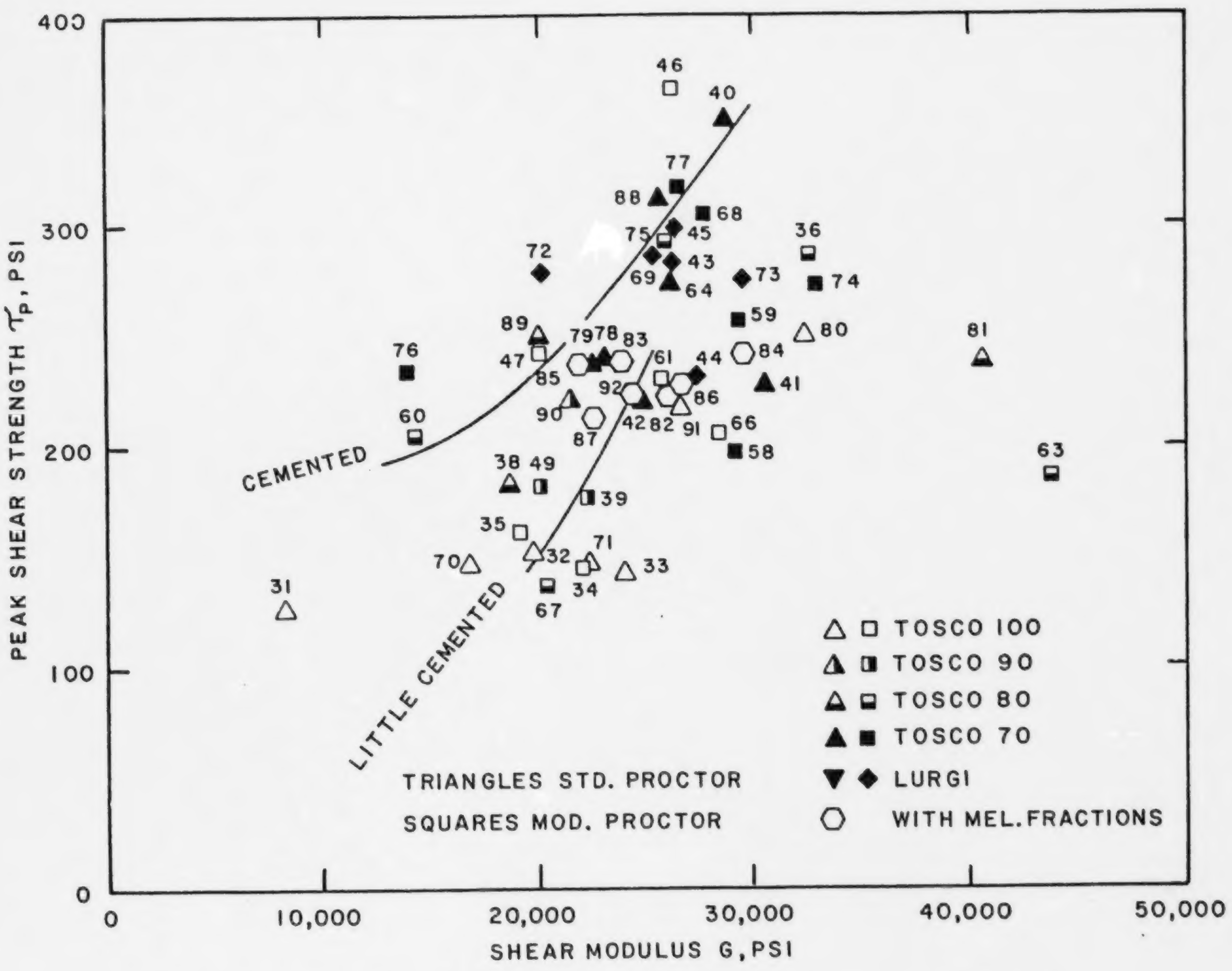


Figure B-II 18. Peak Friction Angle Compared with Initial Shear Modulus G the points plotted in Figure B-II 18 no doubt correspond to specimens with soft tops which too easily sheared and cause displacement of the points downward. Soft tops are caused by poor emplacement of the top pore stone and vanes into the proctor compacted specimen during loading of the spring oedometer.

An apparent higher values of these slow shear moduli for more cemented specimens, suggests that perhaps rapid shear moduli from resonant dynamic tests might be used to nondestructively periodically assay a given curing specimen for cementation. The very small sample needed for an EGA assay suggest this might be periodically done on the specimen also without much altering its integrity for the dynamic test. Perhaps the specimen should be kept under high vertical or high confining pressure to simulate burial even during dynamic G testing. Perhaps it can be shown that proctor compaction is adequate to simulate this and such pressures are unnecessary. With proctor compaction the persistant problem of weak specimen tops would occur. Probably static compaction at the high vertical pressures of interest would simulate a real liner adequately.

Figure B-II 19 plotting BI vs shear modulus G also suggests a distinction between brittle and soft material. Here also some points are no doubt too low.

F. Relation of Peak Friction Angle with Twist at Peak Strength

Figure B-II 20 shows the peak friction angles of the TOSCO 100, 90, 80 and 70 series and the Lurgi material as a function of twist produced during torsion testing at peak strength. There seems to be a trend for greater twist (or strain) before failure for the less compacted standard proctored material than for the more compacted modified proctored material, especially for material giving lower peak friction angles. Greater strain before failure is advantageous in a liner. This does not necessarily correlate positively with tensile strength, however, which has little relation to strain before failure. Tensile strength is more related to shear strength where a rule of thumb says that it is about 1/20 of the shear strength of a cohesive clay soil.

Also plotted in Figure B-II 20 are points for loadings 86 and 92 for a 75% mellowed burned TOSCO - 25% burned TOSCO mix and the point for loading 87 which is of a 50% mellowed burned TOSCO - 50% unburned TOSCO II mix. A large extent of strain before peak strength at low peak friction angles is possible with these mixtures involving mellowed material. In fact this sort of material with low (in these cases negative) brittleness index tends to exhibit simple shear or zone shear and larger twists than those plotted may be more appropriate for this plot since for these materials peak strength does not necessarily imply failure.

G. Relation of Peak Friction Angle and Squashiness With Cured Void Ratio

Figures B-II 21, 22, 23 and 24 show a regularity in peak angle of internal friction plotted vs void ratio for cured TOSCO spent shales, TOSCO

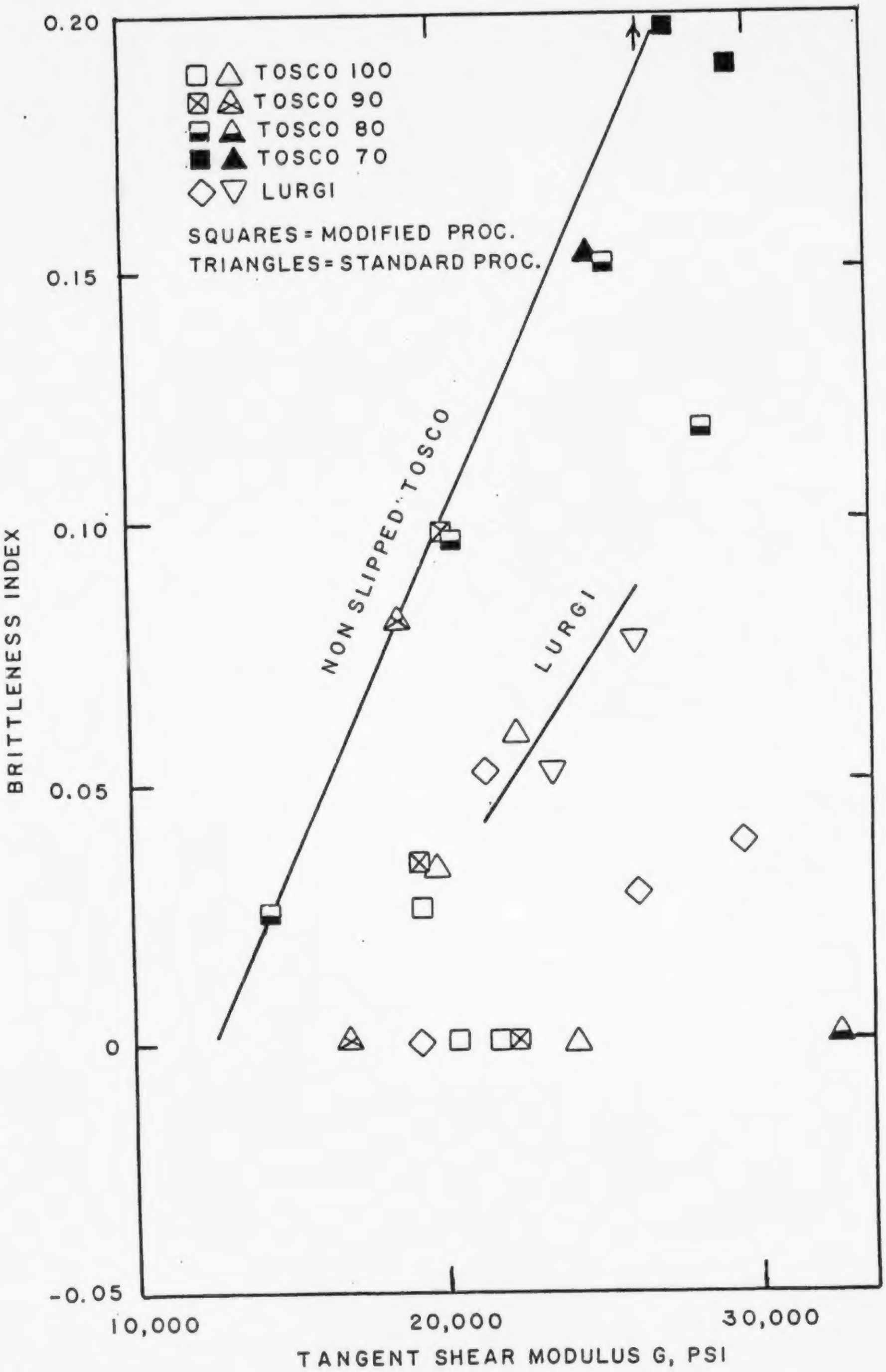


Figure B-II 19. Brittleness Index Compared with Initial Shear Modulus G

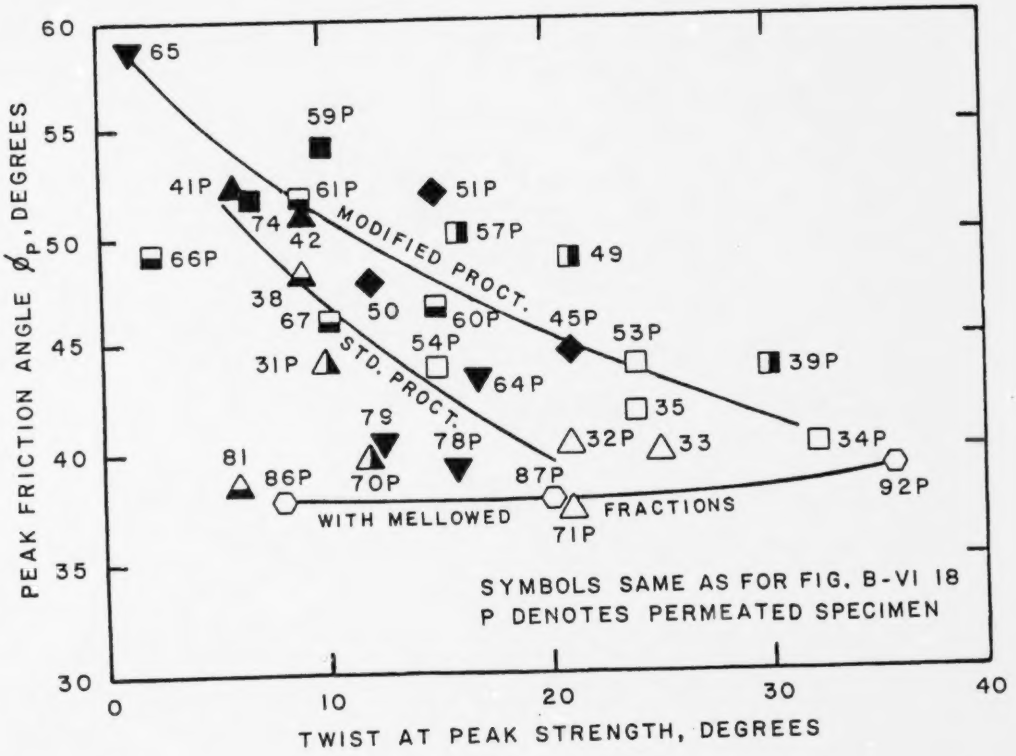


Figure B-II 20. Extent of Twist at Peak Strength Correlated with Peak Friction Angle

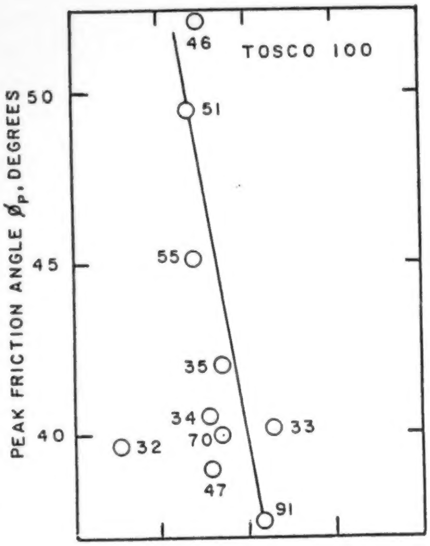


Figure B-II 21. Peak Friction Angle of TOSCO 100 vs Void Ratio

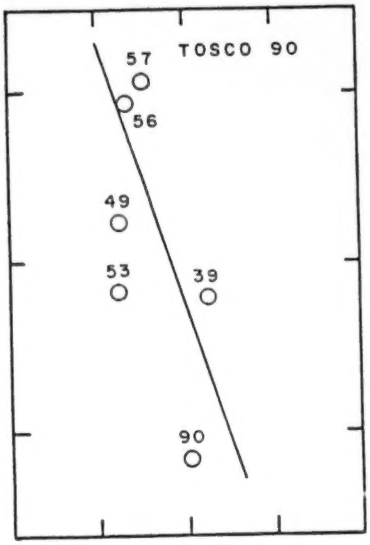


Figure B-II 22. Peak Friction Angle of TOSCO 90 vs Void Ratio

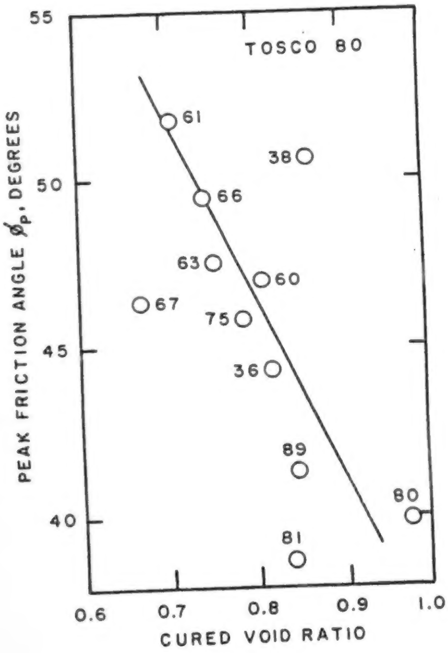


Figure B-II 23. Peak Friction Angle of TOSCO 80 vs Void Ratio

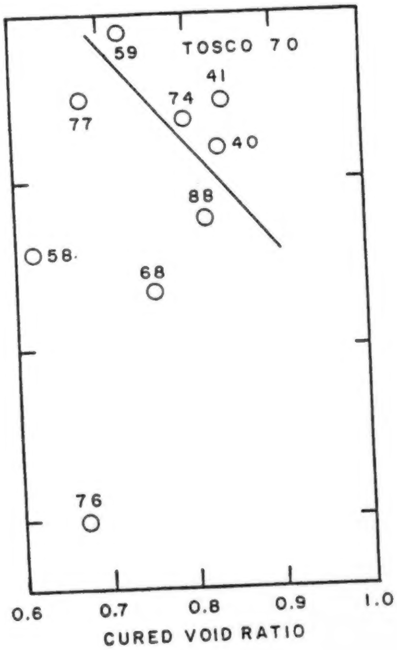


Figure B-II 24. Peak Friction Angle of TOSCO 70 vs Void Ratio

100, 90, 80, and 70, as the fraction of cementaceous burned spent shale increases. Greater void ratios (determined after curing) are associated with lower peak internal friction angles for the TOSCO spent shales. This suggests that a liner made from spent shale should be as little compacted as possible so a lower friction angle and resulting greater squashiness is had which allows better self healing of the rapid type, other factors such as not too much shrinkage at a shear zone being acceptable. The squashiness is inversely proportional to the shear strength which for a silty draining material is $\sigma_v \tan \phi_p$.

H. Hydrate Species Determined by EGA

In the early stages of curing of the series of mixtures TOSCO 100, 90, 80 and 70 rise and fall of an EGA water peak at 115 to 135°C was found. Since both tobernite and ettringite may manefest themselves in this peak some ambiquity exists without x-ray diffraction or other means of distinquishing between them. Figure B-II 25 is a plot of this peak curing time for crumbs of spring oedometer specimens after torsion testing. Timing of this peak is similar to that in development of strength of ϕ_p in Figure B-II 26.

Another EGA water peak at around 225°C becomes prominent with TOSCO 70 material. This is believed to be where the "carbonate ettringite" (ettringite with sulfate replaced by carbonate) manefests itself as an additional part of its EGA curve. The main part, however, still is at the 115 to 135°C peak as for ettringite itself. There is a sudden appearence of the 225°C peak at a sharp threshold with a burned spent shale content below 70%. This suggests that the pH of the water remaining in the mix and/or the carbonate ion concentration level left after some of the alkalinity and carbonate has attacked the unburned TOSCO II spent shale component of the mixture may determine whether ordinary sulfate ettringite or carbonate ettringite is formed. The identification of this peak is substantiated by its reduction in side experiment curings where some gypsum as a source of sulfate is added, its accentuation when Na_2CO_3 is added, and its elimination when $BaCl_2$ or $Ba(NO_3)_2$ as a sulfate scavenger is added.

Figure B-II 27 is a plot of the initial shear modulus G vs the 115 to 135°C EGA peak height for several of the spent shale mixes after curing. Although there is some rise in stiffness at the highest quantities of tobermorite and ettringite found, the effect is not very strong and moreover for low peak heights which are in the low cementation region of most interest the effect is nil. Thus study of cementation of this sort by dynamic G testing does not seem straight forward. It must be recalled that ettringite is not very cementaceous compared to tobermorite and we have not yet analyzed the 115-135°C EGA peak for these.

Figure B-II 28 shows strong inverse correlation of twist at peak strength vs the 115 to 135°C EGA peak height. Several high data points are probably the result of slippage between specimen and upper pore stone. Any cementation produced by these hydrates seems to operate against

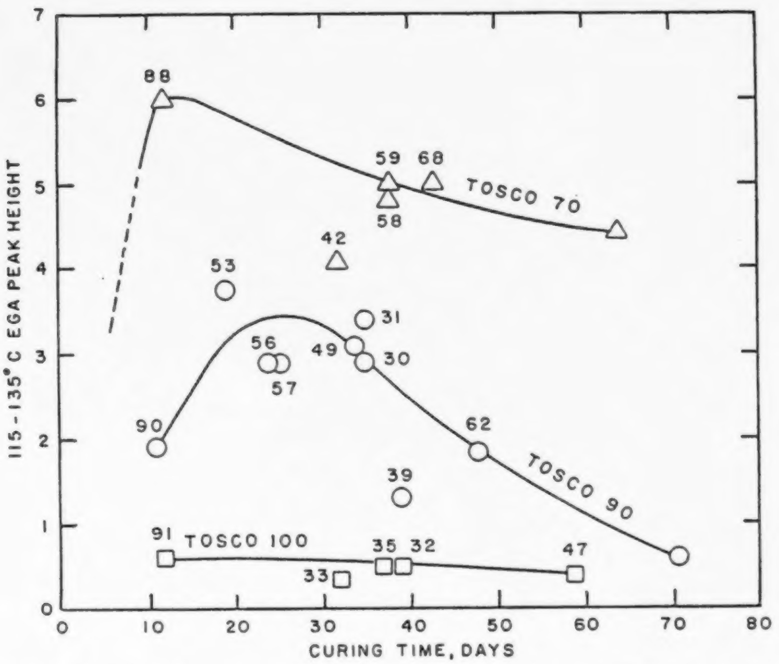


Figure B-II 25. EGA Hydrate Water Peak of Tobermorite and Ettringite vs Time for TOSCO 100, 90, and 70 Specimens

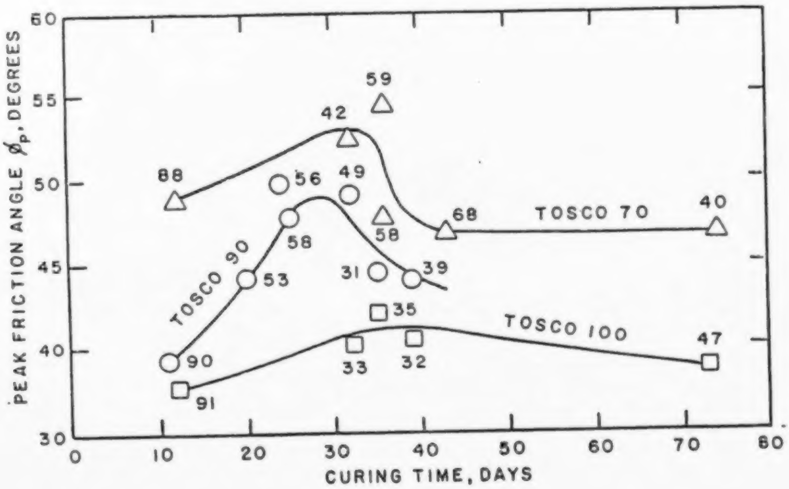


Figure B-II 26. Peak Friction Angle vs Time for TOSCO 100, 90 and 70 Specimens

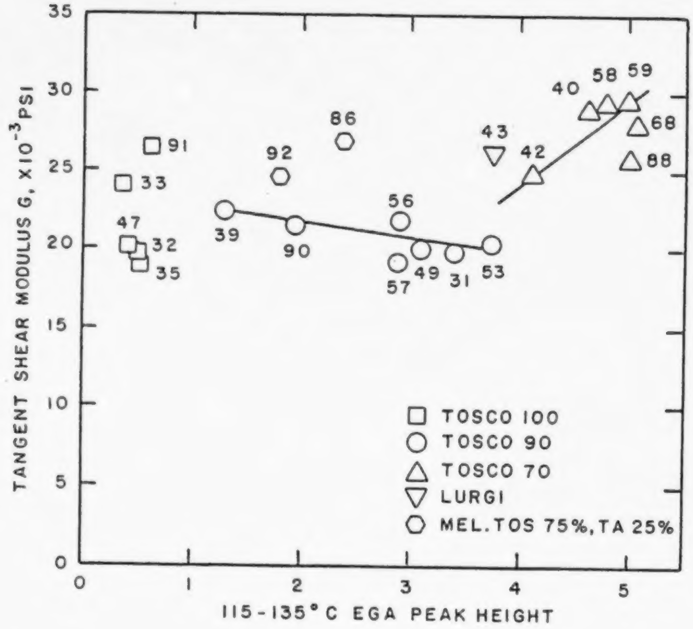


Figure B-II 27. Initial Torsional Stiffness vs 115 to 135°C EGA Peak

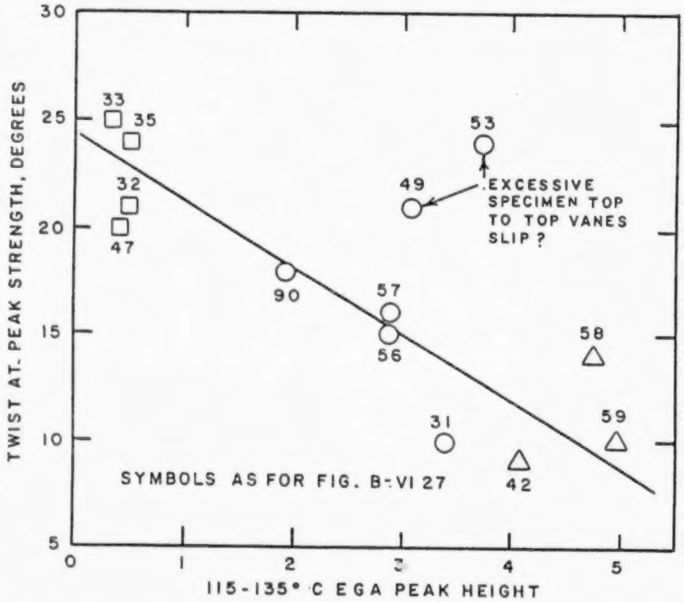


Figure B-II 28. Twist at Peak Strength vs 115 to 135°C EGA Peak Height extensive deformation, the action of interest in self healing, rather than against small deformation involved in initial stiffness.

The peak strength friction angle is quite dependent on the extent of formation of cementaceous hydrates under conditions of the torsion test. Peak strength also correlates fairly well with the void ratio within types of spent shale mixtures such as TOSCO 100, 90, 80, 70 or Lurgi. A better correlation with strength than either of the above should be obtained by plotting the family of void ratio vs peak shear strength curves with the amount of tobermorite water present as a parameter (ignoring any ettringite and hydromagnesite cementing action). The tobermorite might be determined assuming all ettringite is the kind with also a peak at 225°C as well as at 120 to 135°C (carbonate ettringite or hydroxy ettringite but not sulfate ettringite). The early peak at 120 to 135°C or so (depending on its height) results from both tobermorite and ettringite largely superimposed. The tobermorite peak area alone might be obtained by subtracting out a calculated carbonate ettringite area for the 115 to 135°C part of its water evolution calculated from a ratio of the 225°C part of its water evolution.

I. Secondary Compression Index Cα related to Cementation and Mellowing

Figure B-II 29 summarizes Cα, the secondary compression index of the spring oedometer specimens just before the specimens removal from its LVDT height measurement system prior to permeability determination (if made) and torsion testing. In general some specimens showed a uniform height vs log time plot while others showed a fairly sharp downbend in this plot at around of 1 to 5 days as though some kind of friction of cementation were broken loose then in response to a particular environmental change. The nature of these possible clock reactions has not been considered here but should be at some time for whatever type of material might be considered a further possible candidate liner.

Figure B-II 29 shows that at a burned TOSCO spent shale content of about 10% in TOSCO II spent shale shale a minimum Cα occurred for specimens showing a given peak friction angle. Figure B-II 29 is a cross plot of the data shown in Figures B-II 30, 31, 32, 33, 34 and 35 for the last Cα from the LVDT measurements and the peak friction angle later determined by the torsion tester. The scatter of the data in these latter figures is believed to often be due to premature slippage of the specimen at its weaker top rather than failing in a more representative portion in the middle of the specimen. The "best" curves have been drawn through reasonable higher $\emptyset_p$ values of presumed better failed specimens.

It should be commented that none of the Cα values seen to date seem too high for use of a liner for a period of 10,000 years. There is some possibility, however, that the same secondary compression vs log time curves may turn downward even further were specimens studied for longer periods.

The secondary compression index Cα, that can be calcualted from Townsend and Peterson (1979) data for their unscalped TOSCO II spent shale for modified and standard proctor material at 10^4 minutes consolidation

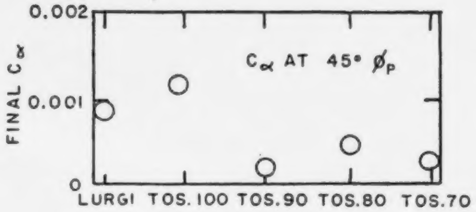
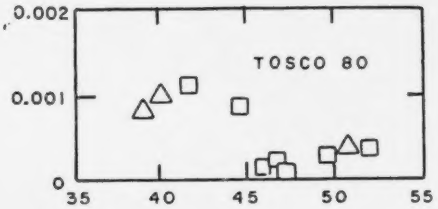
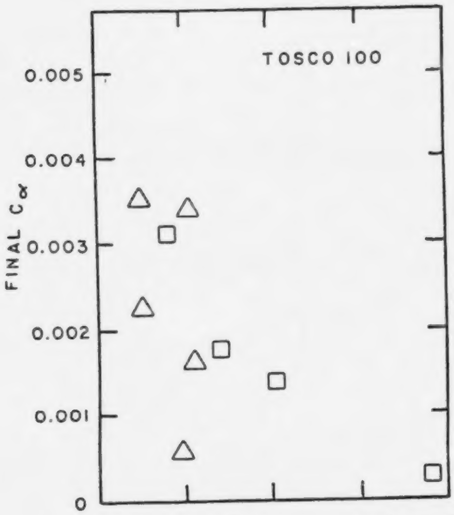


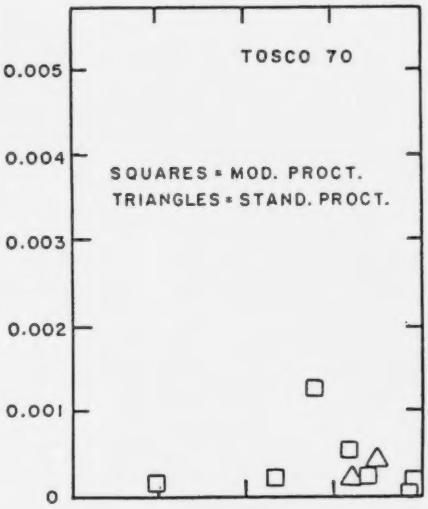
Fig. B-II 29. Final Cα at 45° Peak Friction Angle for Oedometer Specimens of Various Spent Shale



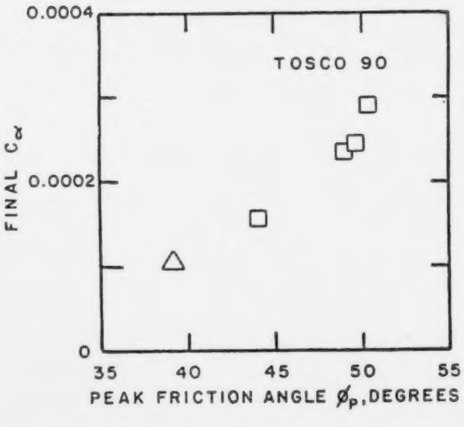
B-II 32. Final Cα vs Peak Friction Angle for TOSCO 80 Specimens



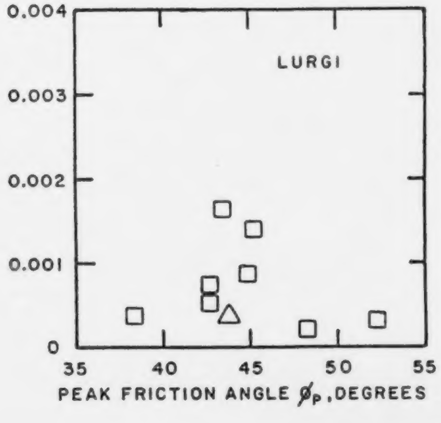
B-II 30. Final Cα vs Peak Friction Angle for TOSCO 100 Specimens



B-II 33. Final Cα vs Peak Friction Angle for TOSCO 70 Specimens



B-II 31. Final Cα vs Peak Friction Angle for TOSCO 90 Specimens



B-II 34. Final Cα vs Peak Friction Angle for Lurgi Specimens and interpolated to a σ_v of 280 psi are about two or three times the values we have found (Figure B-II 30). These higher C_α values would be explained if much of the larger chunks of spent shale in their unscalped sample soften when water soaked so the bridging between them is weakened at their point to point contacts. The ϕ' values reported by these authors for standard and modified proctor are roughly comparable with ϕ_p measured with our torsion apparatus although a number of variables are important to the exact values which are found.

J. Indirect Tensile Strength (Brazilian) Tests

In Figure B-II 35 Brazil indirect tensile strengths of specimens compacted and cured with no confining pressure are compared with the twist at peak strength from the torsion test of counterpart specimens cured in the spring oedometers at around 280 psi vertical pressure and tested near that pressure.

There is a trend in Figure B-II 35 for more cementaceous TOSCO 80 material to give greater tensile strength than less cementaceous TOSCO 90 material and for it to give greater tensile strength than the TOSCO 100 material. Lurgi spent shale gives relatively high tensile strengths while mixtures including mellowed material as noted give low to medium tensile strengths. The negative slope of the trend lines drawn for the different materials suggests that the kind of tensile strength measured by the Brazilian tests is a brittle cementaceous type strength associated with rapid attainment of peak cementaceous shear strength as strain progresses. This slope is opposite to that expected for a correlation of the shear test twist and tensile strength for a cohesive plastic material.

For the silty and sometimes cemented materials of most of the specimens studied here high tensile strength primarily indicates cementation. A more clayish material might show both high twist before peak shear strength and relatively high tensile strength. Tensile strength, as weak as it is, in a material at the overburden depths involved for the liner being considered does not seem to be an important consideration in the face of the high vertical stress involved at depth which greatly increases shear strength.

Figure B-II 36 is a plot of the tensile strain at failure with the Brazil tests vs the twist at peak strength for the torsion tests. It is concluded that only a little cementation reduces the tensile strain at failure considerably. The largest torsion twists (strains) of cemented specimens and less cemented specimens at peak torsion shear strength seen are about the same but the Brazil test tensile strains at tensile failure are much greater for less cementaceous material.

Figure B-II 37 shows some classical shaped tensile strength vs water content curves for specimens made from mixtures involving mellowed materials. Even for the 75% mellowed TOSCO - 25% burned TOSCO specimens which are undergoing some cementation, a peak tensile strength vs water content is observed. The points corresponding to specimen water additions used in the main series of oedometer - torsion tests are indicated by the oedometer loading number of this main series. According to data for these

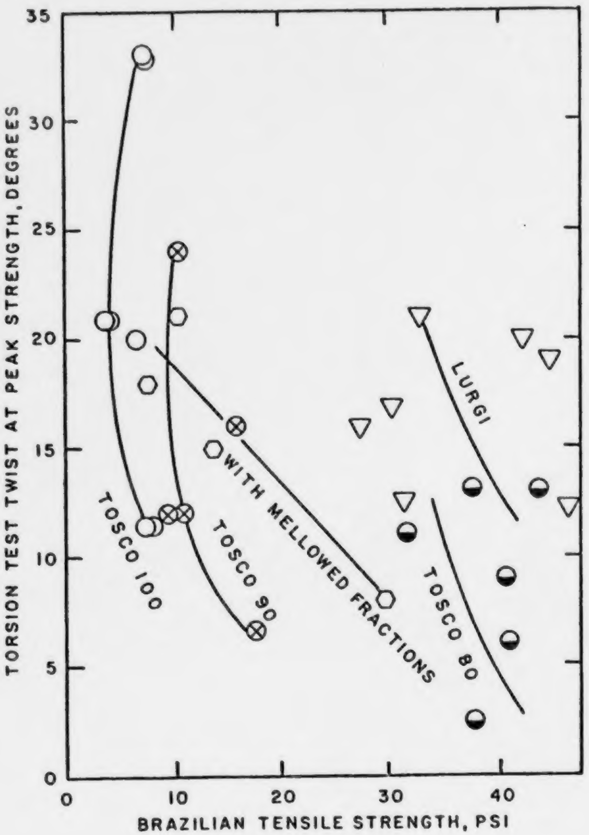


Figure B-II 35. Torsion Test Twist at Peak Strength vs Brazil Tensile Strength

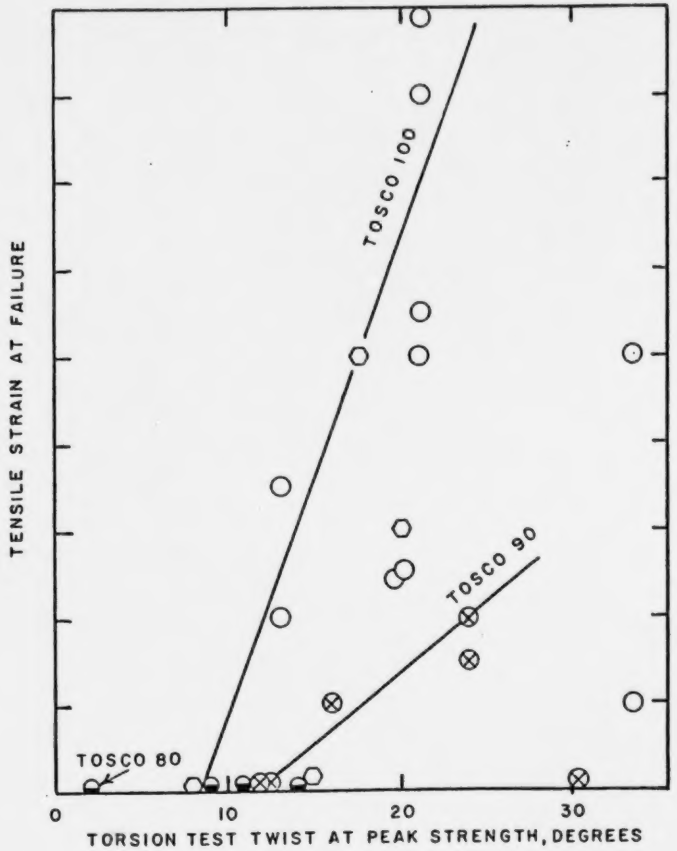


Figure B-II 36. Brazil Tensile Strain At Failure vs Torsion Test Twist at Peak Strength

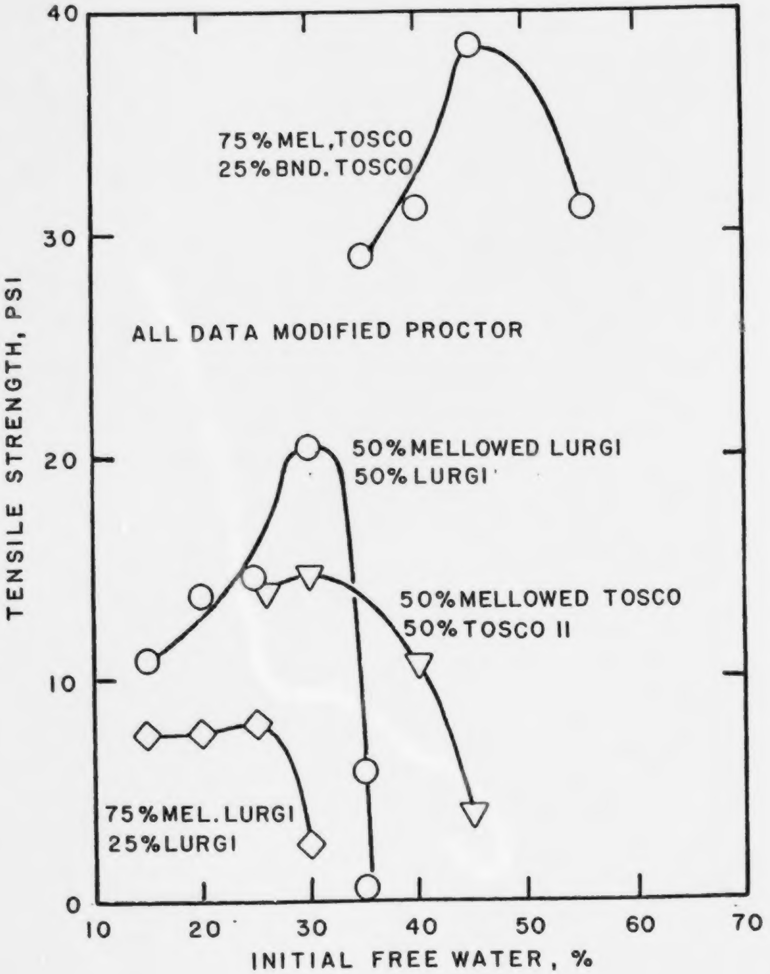


Figure B-II 37. Brazil Tensile Strength vs Initial Water Content

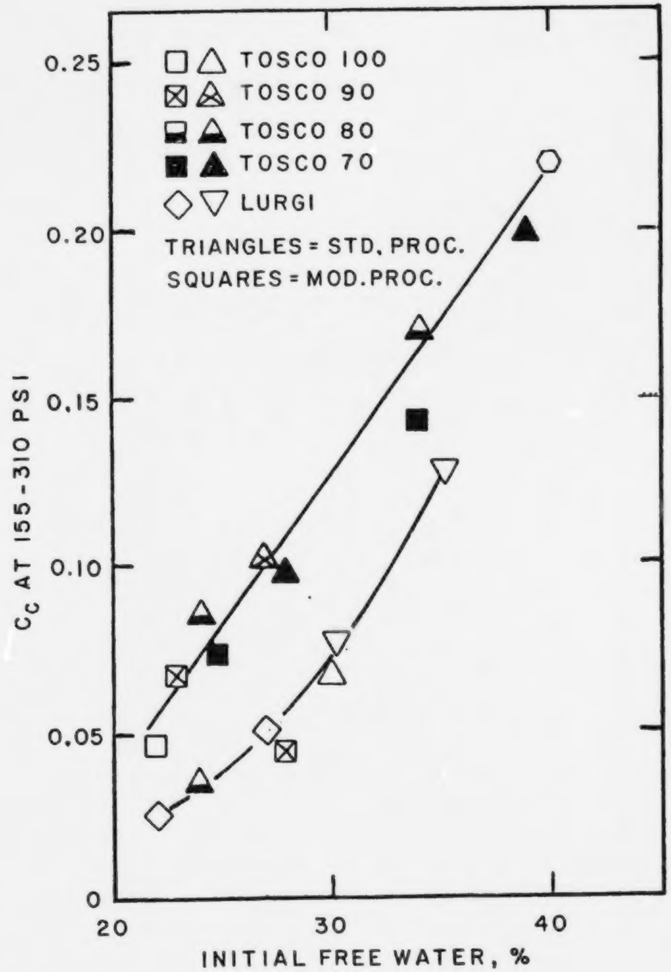


Figure B-II 38. Compression Index of Fresh Specimens for Loading Increment 155 to 310 PSI little aged specimens optimum tensile strength was not usually attained. But as observed above, the properties of the liner is shear at higher vertical pressure which will far over-shadow the weak tensile strengths.

K. Compressibility Coefficients

Pneumatic arm oedometer tests were made on standard proctored or modified proctored specimens one inch high and 2½ inch diameter. Table B-I 1 lists the types of mixes studied by arm oedometer. Table B-II 1 is a summary of some results and some calculations. In the first column t signified TOSCO, m modified proctor, s standard proctor, etc.

Primary consolidation was finished after 80 minutes for the one inch thick double pore stone specimens used. For this time the total compression of the specimen from the data collecting computer print out for each loading increment was read and entered in a computer spread sheet program, Table B-II 1 column D, as steady state Schaevitz units. After converting these to mm compression and correcting for arm oedometer apparatus deflection at the particular load (column C) the net compression was calculated (column F) for that loading increment. Load increments producing vertical pressures on the specimens of 19.4, 38.8, 77.5, 155.0, and 310 psi were used. From the initial water added, mineral grain density of the initial dry mixture before wetting, specimen loaded weight, cell volume of 80.44 cm^3 and specimen top surface area of 31.67 cm^2 the dry densities and void ratio for each loading were calculated and for each change in load the delta void ratio and compression index C_c were calculated (columns K and L).

From the data calculated in Table B-II 1 a variety of correlations may be made. Void ratio e plotted against consolidation stress (load) gives curves typical of silt. Figure B-II 38 shows the compression index for the last loading increment (155 to 310 psi) for each specimen, plotted against the initial water added to the specimen in mixing it. There is much similarity in the position of the curves for the various types of spent shale.

TABLE B-II 1 Pneumatic Arm Oedometer Results from Fresh Specimens: Void Ratios e and Compression Indices C_c

Shale Compac-tion	Initial Water Added,%	Oedometer Deflect Correctn. mm	Initial Schaevitz Units	Steady State Shaevitz Units	Deflect Corrcd Compress. Total mm	Mineral Grain Density gm/cc	Specimen Loaded Weight gm	Dry Density gm/cc	Void Ratio e	Delta Void ratio	Compress Index Cc
t80 s	24	.008	1908	1901	.006	2.786	135.1	1.345	1.056	-.0581	
	24	.030	1908	1879	.028	2.786	135.1	1.355	1.055	.0018	.0059
	24	.050	1908	1854	.058	2.786	135.1	1.357	1.052	.0024	.0080
	24	.065	1908	1821	.109	2.786	135.1	1.360	1.048	.0041	.0137
	24	.075	1908	1758	.225	2.786	135.1	1.366	1.039	.0094	.0312
t70 m	25	.008	1902	1878	.040	2.819	146.7	1.461	0.929	.1096	-
	25	.030	1902	1807	.160	2.819	146.7	1.467	0.920	.0091	.0303
	25	.050	1902	1740	.274	2.819	146.7	1.474	0.911	.0087	.0288
	25	.065	1902	1649	.441	2.819	146.7	1.484	0.898	.0127	.0422
	25	.075	1902	1501	.727	2.819	146.7	1.501	0.877	.0217	.0722
t70 s	28	.008	1914	1906	.008	2.819	139.3	1.353	1.083	-.2061	-
	28	.030	1914	1856	.086	2.819	139.3	1.357	1.076	.0064	.0212
	28	.050	1914	1793	.192	2.819	139.3	1.362	1.068	.0087	.0289
	28	.065	1914	1692	.379	2.819	139.3	1.373	1.052	.0153	.0509
	28	.075	1914	1504	.745	2.819	139.3	1.393	1.022	.0300	.0993
t70 m	34	.008	1868	1809	.110	2.819	144.5	1.346	1.094	-.0711	-
	34	.030	1868	1700	.306	2.819	144.5	1.356	1.077	.0162	.0539
	34	.050	1868	1602	.482	2.819	144.5	1.366	1.063	.0146	.0484
	34	.065	1868	1439	.793	2.819	144.5	1.383	1.037	.0257	.0855
	34	.075	1868	1174	1.313	2.819	144.5	1.413	0.994	.0430	.1429
lurgi m	22	.008	1925	1917	.008	2.622	137.1	1.397	0.876	.1179	-
	22	.030	1925	1894	.032	2.622	137.1	1.398	0.874	.0017	.0059
	22	.050	1925	1868	.064	2.622	137.1	1.400	0.872	.0023	.0079
	22	.065	1925	1841	.103	2.622	137.1	1.402	0.869	.0029	.0096
	22	.075	1925	1786	.203	2.622	137.1	1.408	0.862	.0074	.0245

Table B-II 1. (CONT'D)

Shale Compac-tion	Initial Water Added,%	Oedometer Deflect Correctn. mm	Initial Schaevitz Units	Steady State Shaevitz Units	Deflect Corrcd Compress. Total mm	Mineral Grain Density gm/cc	Specimen Loaded Weight gm	Dry Density gm/cc	Void Ratio e	Delta Void ratio	Compress Index Cc
lurg s	30	.008	1883	1849	.060	2.622	143.2	1.372	0.910	-.0484	-
	30	.030	1883	1768	.200	2.622	143.2	1.380	0.899	.0105	.0350
	30	.050	1883	1701	.314	2.622	143.2	1.386	0.891	.0086	.0285
	30	.065	1883	1617	.467	2.622	143.2	1.394	0.879	.0115	.0383
	30	.075	1883	1458	.775	2.622	143.2	1.412	0.856	.0232	.0771
lurg m	27	.008	1966	1952	.020	2.622	145.3	1.423	0.842	.0143	
	27	.030	1966	1910	.082	2.622	145.3	1.426	0.837	.0045	.0149
	27	.050	1966	1858	.166	2.622	145.3	1.431	0.831	.0061	.0202
	27	.065	1966	1790	.287	2.622	145.3	1.438	0.823	.0088	.0292
	27	.075	1966	1683	.491	2.622	145.3	1.450	0.808	.0148	.0492
t50/50 m	40	.008	1920	1889	.054	2.724	131.4	1.169	1.330	-.5218	-
	40	.030	1920	1809	.192	2.724	131.4	1.175	1.317	.0127	.0421
	40	.050	1920	1648	.494	2.724	131.4	1.189	1.289	.0277	.0922
	40	.065	1920	1413	.949	2.724	131.4	1.211	1.247	.0418	.1388
	40	.075	1920	1053	1.659	2.724	131.4	1.248	1.182	.0652	.2166
t100 m	22	.008	1940	1927	.018	2.72	147.1	1.49 !	0.813	.0000	-
	22	.030	1940	1891	.068	2.72	147.1	1.502	0.810	.0036	.0119
	22	.050	1940	1842	.146	2.72	147.1	1.507	0.804	.0056	.0185
	22	.065	1940	1778	.259	2.72	147.1	1.514	0.796	.0081	.0268
	22	.075	1940	1680	.445	2.72	147.1	1.525	0.783	.0132	.0441
t100 s	25	.008	1822	1784	.068	2.72	136.4	1.360	0.9 8	-.2154	-
	25	.030	1822	1655	.304	2.72	136.5	1.373	0.980	.0186	.0618
	25	.050	1822	1502	.590	2.72	136.5	1.389	0.957	.0225	.0749
	25	.065	1822	1308	.963	2.72	136.5	1.410	0.928	.0294	.0977
	25	.075	1822	1051	1.467	2.72	136.5	1.440	0.888	.0397	.1319

Table B-II 1. (CONT'D)

Shale Compac-tion	Initial Water Added,%	Oedometer Deflect Correctn. mm	Initial Schaevitz Units	Steady State Shaevitz Units	Deflect Corrcd Compress. Total mm	Mineral Grain Density gm/cc	Specimen Loaded Weight gm	Dry Density gm/cc	Void Ratio e	Delta Void ratio	Compress Index Cc
t90 m	23	.008	1885	1867	.028	2.753	149.2	1.509	0.823	.0644	-
	23	.030	1885	1820	.100	2.753	149.2	1.513	0.818	.0052	.0172
	23	.050	1885	1748	.224	2.753	149.2	1.521	0.809	.0089	.0296
	23	.065	1885	1651	.403	2.753	149.2	1.531	0.797	.0129	.0421
	23	.075	1885	1509	.677	2.753	149.2	1.548	0.777	.0197	.0654
t90 s	27	.008	1930	1919	.014	2.753	138.7	1.358	1.026	-.2496	-
	27	.030	1930	1866	.058	2.753	138.7	1.360	1.023	.0035	.0117
	27	.050	1930	1819	.172	2.753	138.7	1.366	1.014	.0091	.0302
	27	.065	1930	1706	.383	2.753	138.7	1.378	0.997	.0168	.0559
	27	.075	1930	1512	.761	2.753	138.7	1.399	0.967	.0302	.1002
t90 m	28	.008	1750	1726	.040	2.753	146.2	1.421	0.936	.0312	-
	28	.030	1750	1688	.094	2.753	146.2	1.424	0.932	.0041	.0137
	28	.050	1750	1638	.174	2.753	146.2	1.429	0.925	.0061	.0202
	28	.065	1750	1568	.299	2.753	146.2	1.436	0.916	.0095	.0317
	28	.075	1750	1478	.469	2.753	146.2	1.446	0.903	.0129	.0431
t80 s	24	.008	1878	1859	.030	2.786	135.0	1.354	1.056	-.1529	-
	24	.030	1878	1815	.096	2.786	135.0	1.358	1.051	.0053	.0178
	24	.050	1878	1761	.184	2.786	135.0	1.363	1.043	.0071	.0237
	24	.065	1878	1672	.347	2.786	135.0	1.371	1.030	.0132	.0439
	24	.075	1878	1514	.653	2.786	135.0	1.388	1.005	.0248	.0823
t100 s	20	.008	1849	1838	.014	2.720	131.0	1.347	1.003	.0675	-
	20	.030	1849	1820	.028	2.720	131.0	1.348	1.002	.0011	.0037
	20	.050	1849	1786	.076	2.720	131.0	1.360	0.9 8	.0038	.0126
	20	.065	1849	1738	.157	2.720	131.0	1.365	0.992	.0064	.0212
	20	.075	1849	1632	.359	2.720	131.0	1.376	0.976	.0159	.0529

TABLE B-II 1. (Cont'd)

Shale Compaction	Initial Water Added,%	Oedometer Deflect Correctn. mm	Initial Schaevitz Units	Steady State Shaevitz Units	Deflect Corrcd Compress. Total mm	Mineral Grain Density gm/cc	Specimen Loaded Weight gm	Dry Density gm/cc	Void Ratio e	Delta Void ratio	Compress Index Cc
t90 s	22	.008	1821	1797	.040	2.753	136.0	1.387	0.983	-.0075	-
	22	.030	1821	1767	.078	2.753	136.0	1.389	0.980	.0029	.009 !
	22	.050	1821	1714	.164	2.753	136.0	1.394	0.974	.0067	.0223
	22	.065	1821	1634	.309	2.753	136.0	1.402	0.962	.0113	.0376
	22	.075	1821	1465	.637	2.753	136.0	1.421	0.937	.0256	.0852
t 80 s	29	.008	1885	1815	.132	2.786	143.0	1.385	1.011	-.0744	-
	29	.030	1885	1748	.244	2.786	143.0	1.391	1.022	.0089	.0296
	29	.050	1885	1629	.462	2.786	143.0	1.403	0.985	.0173	.0576
	29	.065	1885	1471	.763	2.786	143.0	1.420	0.961	.0239	.0795
	29	.075	1885	1246	1.203	2.786	143.0	1.446	0.926	.0349	.1163
t 70 s	33	.008	1891	1823	.128	2.819	140.4	1.318	1.137	-.2113	-
	33	.030	1891	1753	.246	2.819	140.4	1.324	1.127	.0099	.0331
	33	.050	1891	1615	.502	2.819	140.4	1.338	1.106	.0216	.0719
	33	.065	1891	1415	.887	2.819	140.4	1.359	1.073	.0325	.1081
	33	.075	1891	1123	1.461	2.819	140.4	1.392	1.024	.0485	.1612
lurgi s	40	.008	1909	1886	.038	2.622	137.7	1.224	1.141	-.1166	-
	40	.030	1909	1851	.086	2.622	137.7	1.226	1.137	.0040	.0135
	40	.050	1909	1785	.198	2.622	137.7	1.232	1.128	.0094	.3134
	40	.065	1909	1700	.353	2.622	137.7	1.239	1.114	.0131	.0434
	40	.075	1909	1579	.585	2.622	137.7	1.251	1.095	.0196	.0650
1 75/25s	25	.008	1957	1927	.052	2.665	142.2	1.416	0.880	.2145	-
	25	.030	1957	1871	.142	2.665	142.2	1.421	0.874	.0067	.0222
	25	.050	1957	1795	.274	2.665	142.2	1.429	0.864	.0098	.0325
	25	.065	1957	1695	.459	2.665	142.2	1.439	0.850	.0137	.0456
	25	.075	1957	1531	.777	2.665	142.2	1.458	0.827	.0236	.0783

III. CONCLUSIONS AND RECOMMENDATIONS

1. A softer less brittle material after placement seems desirable for most of the specimens tested. Apparently the angularity and harshness of silt and sand sized particles in most mixes is the cause of a relatively high angle of internal friction for the peak shear strengths and residual shear strengths found after yielding. Such high strengths do not seem necessary nor desirable and should be traded off for lower angles of friction through less compaction, some heap mellowing time which will allow more particle surface roughening and floculation and looser compaction while retaining some measure of swelling and shrinkage stability, and/or addition or generation of some quantity of clayish material. The latter can apparently be made from certain spent oil shales by autoclave mellowing but it may be more economical to add clay from other sources. Trial of further autoclave mellowed or other mellowed materials seems desirable.

2. Trial of addition of clay or other similar fines to reduce permeability in the case of the TOSCO II spent shale or the average Lurgi spent shale is desirable. This could be an added component or could be generated from autoclaving an especially active burned spent shale such as the burned TOSCO material.

3. Ring shear tests should be made to get ϕ_R at large displacements for several examples of candidate liner material.

4. The cementing characteristics of burned spent shale seem to be a detriment to self healing as any shear movement needed for closure of a vertical tension crack by "caving in" of liner material would produce shear plane separated fragments. The planes may be possible water channels. Moreover the depth into the liner away from the tension crack for a source of fill material will be less for high shear strength liner material. Extrusion of a non brittle plastic liner material, into a tension crack, on the other hand, should not produce such distinct planes. Autoclave mellowing inhibits cementation of materials.

5. The high friction angles observed in most of the liner specimens tested are useful in that there will be less tendency for a pile of spent oil shale founded on a liner to slip down a valley. Silty sandy materials producing high friction angles are generally rather permeable and uncemented specimens of the materials here tested are no exception. To reduce permeability clay sized material can be mixed in or a non strength producing fine precipitate or colloid within the interstitial spaces of the silt grains might conceivably be internally generated. In this way a synthetic boulder clay having both low permeability yet a reasonably high friction angle might be produced.

6. Quick clay inadvertently made in any of the above ways should be avoided. Even a material that has only a little above critical void volume should be suspect until proven unlikely to soften or liquify when subjected to slip or earthquake produced shear. Even though a liner material in unsaturated condition may not soften or liquify the same material when

saturated may soften under shear strains. This must be predictable and eventually probably must be studied for any candidate liner material.

7. The "final" secondary compression rates or $C\alpha$ for none of the materials, when measurements ceased just before torsion testing, was excessive. Rates below 2% settlement at 10,000 years by extrapolation were about as large as observed. Much lower rates were more typical. However since the settlement vs log time curves plotted were often concave downward specimens should be followed for longer periods and chemistry of the apparent softening with age ascertained.

8. The effect of additives on spent shale should be further studied in a more methodical experimental design. Gradations of mixes between silty spent shale and clayish material should be tested for the following:

1. Permeability
2. Shear strength by a quick method relative to the permeability so any softening due to reduction of soil skeleton volume during shear is observable.
3. Shear strength of both saturated and unsaturated material should be studied.

Well mixed or pugged materials should be used or fines should be generated internally.

9. Possible methods for in situ fines generation include the following:

a. Mix two slow precipitating liquid intereactants in with the spent shale.
b. Mix in one liquid reactant which reacts with the spent shale itself.
c. Mix in a solid reactant which reacts with the spent shale.

The spent shale base for the mixture should not be burned spent shale to avoid the cementation already demonstrated but one such as TOSCO II material. Perhaps mildly autoclave mellowed burned spent shale would not cement even though much ettringite may be initially formed.

10. Periodic non destructive resonant measurement of shear modulus G may be valuable for following development of any cementation in a given specimen as curing or aging procedes. EGA and to a lessor degree x-ray diffraction may also be done on the same specimen without affecting G since such small samples are required.

11. Experiments with physical models of liner materials should be made in which a tension crack is induced in brittle containment strata and the ability of liner material to suppress water flow as the crack opens is measured. It is desirable to be able to perform meaningful experiments of this sort without the need for continuous high vertical pressures during aging of the liner. Strong forces at the time of, say, flexing or stretching a model to generate a tension crack would, of course be necessary however. Proof is desirable that proctor or other compacted liner material in such a model approximates a real liner aged with considerable overburden pressure.

IV. REFERENCES

Ingles, O.G., "Soil Chemistry Relevant to the Engineering Behavior of Soils" in I.K. Lee, Editor, Soil Mechanics Selected Topics, American Elsevier Publishing Co., Inc., New York 1968.

Townsend, F.C. and R.W. Peterson, Geotechnical Properties of Oil Shale Retorted by the Paraho and TOSCO Processes, Tech. Rept. GL-79-22, Geotechnical Laboratory, U.S. Army Engineer Waterways Experiment Station. Vicksburg Miss. For U.S. Dept. of Interior, Bur. of Mines, Spokane Mining Research Center, Spokane Wash. Under Contract No. H0262064.